VOL. XIX. 1911

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OF THE

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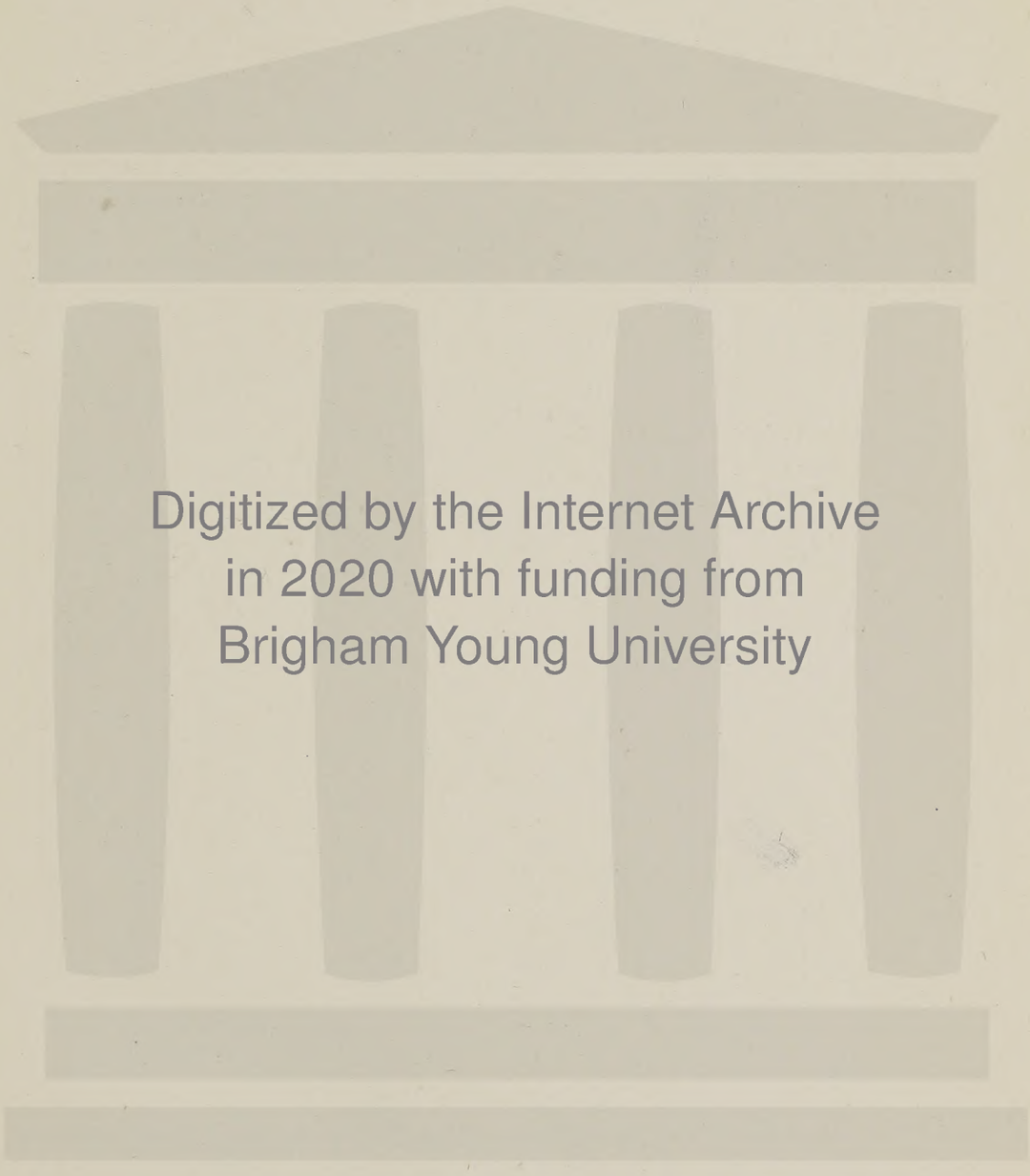

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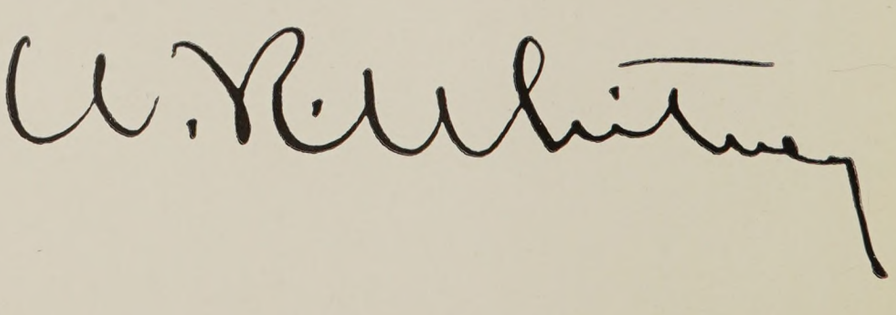

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TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

VOLUME XIX.

157551

NINETEENTH GENERAL MEETING

NEW YORK CITY, APRIL 6, 7, 8, 1911.

PUBLISHED BY
THE AMERICAN ELECTROCHEMICAL SOCIETY
LEHIGH UNIVERSITY, SOUTH BETHLEHEM, PA.
1911

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TABLE OF CONTENTS

PAGE

Portrait of President W. R. Whitney, Ph. D.....Frontispiece
Proceedings of the Nineteenth General Meeting..... 1
Annual Report of the Board of Directors..... 8
Annual Report of the Secretary..... 9
Annual Report of the Treasurer..... 12
List of Members and Guests in Attendance at Nineteenth Meeting....12
New Members, December, 1910, to April, 1911.....15

ADDRESS.

Chemical Research and Industrial Progress—President W. R. Whitney 17

PAPERS.

Dry Cell Testing—W. B. Pritz..... 31
The Tate Bifunctional Accumulator Plate—Alfred O. Tate..... 47
Some Unsolved Problems in Electroplating—George B. Hogaboom.... 53
The Electrolytic Corrosion of Electroplated Objects—Walter S. Landis 59
Mercurous Perchlorate Electrolytic Meter—Frank C. Mathers and Albert F. O. Germann 69
Electrical Heating as a Means of Prevention of Superheating of Liquids —J. Howard Mathews 81
Polarization in its Relation to the Decomposition Pressure of Electrolytes—Oliver P. Watts 91
Electric Discharges in Gases at Reduced Pressure—Louis A. Parsons..109
The Mechanism of Electrolytic Transfer—Joseph W. Richards.....119
The Electrolytic System of Amalgamating Gold Ores—Elmer Ellsworth Carey 127
The Clancy Electrochemical Cyanide Process—John Collins Clancy...137
Some Observations on Laboratory Production of Aluminium—H. K. Richardson 159
An Electrolytic Furnace Method for Producing Metals—John Woods Beckman 171
Electrolytic Refining as a Step in the Production of Steel—Charles F. Burgess 181

PAGE

The Reliability of Electric Furnaces for Commercial Work—Fred T. Snyder 185

The Electric Furnace for the Manufacture of Iron and Steel—James Lyman 193

A Few Experiences with the 15-Ton Héroult Electric Furnace at South Chicago—C. G. Osborne 205

Electric Steel Processes as Competitors of the Bessemer and Open Hearth—Albert E. Greene 233

A New Type of Electric Furnace—Carl Hering 255

A New Electric Resistance Furnace—Francis A. J. FitzGerald 273

An Electric Furnace for Heating Bars and Billets—Thaddeus F. Baily. 285

A Replaceable Unit System of Electric Heating Apparatus—Milton M. Kohn 299

The Johnson Electric Zinc Furnace—Joseph W. Richards 311

The Condensation of Zinc Vapor from Electric Furnaces—F. T. Snyder. 317

Electrically Fused Alumina—"Alundum"—as a Refractory—L. E. Saunders 333

The Advantages of Keokuk, Iowa, for Electrochemical Industries—Frank P. H. Knight 345

The Advantages of Maine for Electrochemical Industries—C. Vey Holman 351

On the Relation of Surface Action to Electrochemistry—Harrison E. Patten 359

The Clancy Electrochemical Cyanide Process—*Belated Discussion* 381

Index 383

Advertisements .....

ERRATUM

Page 223, Line 1, Osorne should read Osborne.

VOLUME XIX. 1911.

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE NINETEENTH GENERAL MEETING OF THE SOCIETY, HELD IN NEW YORK CITY, APRIL 6, 7, 8, 1911.

Number of members registered, 212; guests, 149; total, 361.

PROCEEDINGS OF THURSDAY, APRIL 6th.

The Board of Directors met at 9.00 A. M. in the Board Room of the new Chemists' Club Building, 50 East 41st Street. The annual report of the Secretary and Treasurer made at that meeting will be found printed at the end of these Proceedings.

The Annual Business Meeting of the Society was called to order at 10.00 A. M. in the Rumford Auditorium of the new Chemists' Club Building, Dr. Wm. H. Walker, President, in the Chair. Dr. Walker spoke as follows:

"It is both a privilege and a pleasure to call this, our Nineteenth General Meeting, to order. The occupancy of this building, with all its fine arrangements, records a step in advance in the science of chemistry in its different ramifications. It is for community of interests, the kind of community which makes for progress; and with an expression of our kind appreciation, the appreciation which the Society feels towards the men who made this building possible, and also for the privilege of occupying it for our meetings, I would declare our Nineteenth General Meeting now open."

The reading of the Minutes of the Eighteenth General Meeting

was dispensed with, and they were approved as published in the Transactions, Volume XVIII.

The report of the Board of Directors, including those of the Secretary and Treasurer, was read by the Secretary and accepted for publication in the proceedings of the meeting, to which it is appended.

The above reports show a total membership of 1,211 at the close of 1910, a net gain of 145 during that year. Also a surplus of receipts above expenses of $1,176.40 during 1910, of which $1,049.86 was added to permanent investment account. The net assets of the Society at the close of 1910 were: Cash on hand, $1,117.13; Permanent Investment, $3,548.61; Total, $4,565.74.

The Secretary reported also the total membership at the date of this meeting, including 54 members elected but not yet qualified, as 1,324, and the present net assets as $6,393.82.

The report of the annual election for president, three vice-presidents, three managers, treasurer and secretary was then, in the absence of the tellers, opened by the Secretary and read as follows:

REPORT OF THE TELLERS OF ELECTION.

To the American Electrochemical Society:

GENTLEMEN: Following is the result of the count of ballots for officers of the American Electrochemical Society:

For President—W. R. Whitney, 257; F. J. Tone, 41.

For Vice-Presidents—E. F. Smith, 241; F. A. J. FitzGerald, 204; A. von Isakovics, 184; S. A. Tucker, 122; E. R. Taylor, 99; W. D. Bancroft, 1; E. A. Sperry, 1.

For Managers—W. D. Bancroft, 219; Carl Hering, 179; E. G. Acheson, 136; F. J. Tone, 76; C. J. Russell, 74; E. A. Sperry, 66; H. R. Carveth, 49; A. B. Marvin, 25; J. W. Brown, 24; L. E. Saunders, 24; H. B. Coho, 1; E. F. Smith, 1.

For Treasurer—Pedro G. Salom, 295.

For Secretary—J. W. Richards, 293; P. McN. Bennie, 1; W. S. Landis, 1.

Respectfully submitted,

W. S. FRANKLIN, *Chairman.*
S. S. SEYFERT,
W. S. LANDIS.

South Bethlehem, Pa.,
March 29, 1911.

The Chairman then announced that, in accordance with the Report of the Tellers, he declared as elected the following:

President (for one year)—W. R. Whitney.

Vice-Presidents (for two years)—E. F. Smith, F. A. J. Fitz-Gerald, A. von Isakovics.

Managers (for three years)—W. D. Bancroft, Carl Hering, E. G. Acheson.

Treasurer (for one year)—Pedro G. Salom.

Secretary (for one year)—Jos. W. Richards.

On April 29th, the Board of Directors elected S. A. Tucker as Manager, to fill the unexpired term of Dr. W. R. Whitney, vacant because of the latter's election as president.

President Wm. H. Walker then called upon the President-elect Whitney, whom he presented to the Society and who spoke as follows:

"I will not take any of your time in talking, but will take this opportunity to read a few lines from Browning, which I brought with me in case of my failure of election. This is no new experience, for me to run as a candidate for the position of President of this Society, and I prepared these remarks in case I should have failed. I did not prepare anything in case I should succeed in being elected. These lines were sent to me by a dear friend the other day,—I do not know whether it had any bearing on this occasion—but these lines of Browning fit so well on the present occasion, and I am such a great admirer of Browning (where I can understand him at all, which is not often) that I beg your indulgence in reading these lines to you:

> "'Then welcome, each rebuff
> Which turns earth's smoothness rough;
> Each sting, that bids nor sit, nor stand, but go.
> Be our joys three parts pain—
> Strive and hold cheap the strain;
> Learn, nor account the pang;
> Dare, never grudge the throe.
> For thence—a paradox
> Which comforts, while it mocks—
> Shall life succeed, in that it seems to fail.'

"I want to say that I shall be glad to serve this Society as best I can as President during the coming year.

"What I want to stand for is any kind of improvement—universal optimism. The American people is a young race of people, the American chemists are a young kind of chemist, and have a lot to learn, but an optimistic spirit will be one of the best tools that we can have in our possession. It takes the place of a large quantity of gray matter—there is no doubt about that in my mind. I sometimes say I would rather have a certain quantity of optimism than the same quantity of gray matter. A man who has optimism in his make-up has a wonderful tool in his possession. An optimist does not tell you that a thing will succeed; he says, with enthusiasm, 'Go ahead and try it—see what it will do.'

"I was talking with a man who is not an optimist the other day, who had been losing money. He figured out that the chances of a coin coming 'head' five times in succession were so small that he was willing to bet, the coin having come four times 'heads,' that there was but a very small chance of its coming 'heads' the fifth time. Now, the chance of its coming 'heads' after it had come 'heads' four times is as great as ever—the optimist must look at things in that way. There is an even chance all the time, and we had better take that chance.

"I was reading a portion of Faraday's works the other day, in which he described a 'beautiful experiment,'—he said, 'Here is a beautiful thing.' In using this language he pointed out something which set me thinking. He was talking about ions, and found that certain things affected ions. He said, 'It is of the utmost importance for us to determine as soon as possible what these things are—barium, phosphorus, nitrogen, aluminum, chromium, etc.' Now just think, since that date, 1837, of what has been done in the electrochemical industry. The average chemist will say in his innocence that carbon will not dissolve in anything, and if it did it would not harmonize. I say, you had better try it, that the chances are somebody will find it out. The new things are the things to be tried; not those that seem best to us all the time."

President Walker then announced that the Society had received a very cordial invitation from the Regents of the University of Toronto, and the Canadian Section of the Society of Chemical Industry, through one of our Managers, Dr. W. Lash Miller, to hold the Fall Meeting of the Society in Toronto. This invitation

has been accepted by the Board of Directors and the Fall Meeting will be held in Toronto, Canada, September 21, 22 and 23.

The business part of the session being concluded, the reading and discussion of papers were taken up as follows:

Papers were read by L. E. Saunders, F. A. J. FitzGerald, M. M. Kohn, T. F. Baily and Jos. W. Richards, and discussed, as printed in full in these Transactions.

The afternoon was devoted to an excursion to the works of the Nichols Copper Company, at Laurel Hill, Brooklyn, N. Y., the largest copper refining plant in the world. Over 100 members and guests took part in this excursion.

The evening of April 6th was occupied by a very enjoyable dinner *en famille,* in the dining room of the new Chemists' Club, in which nearly 100 members and guests participated and thoroughly enjoyed themselves.

PROCEEDINGS OF FRIDAY, APRIL 7th.

The meeting was called to order at 10.00 A. M. in the Rumford Auditorium of the new Chemists' Club.

Papers by J. C. Clancy, E. E. Carey, C. F. Burgess, W. S. Landis, Geo. A. Hogaboom, O. P. Watts, J. H. Mathews, A. O. Tate, H. K. Richardson, F. C. Mathers and A. F. O. Germann (abstracted by Carl G. Schluederberg), L. A. Parsons and Jos. W. Richards, were presented and discussed, as printed in full in these Transactions.

The afternoon was devoted to three alternate visits.

The first to the electroplating plant of Hanson and Van Winkle Company, at Newark, N. J., to inspect their demonstrating electroplating plant, used for demonstrating their mechanical apparatus for electroplating large quantities of work in bulk.

The second visit included the inspection of the laboratory of Dr. F. J. Maywald and the plant of the Moss Engraving Company, the former comprising various types of electric furnaces for laboratory use; the latter being a large plant for plating, engraving and using electrotyping processes.

The third visit was to the New York Electrical Testing Laboratory, the Laboratories of the College of the City of New York and of the Columbia University.

The first visit was conducted by Prof. J. W. Richards; the

second by Mr. Bedell, of the staff of *Metallurgical and Chemical Engineering;* the third by Dr. H. R. Moody, of the College of the City of New York.

In the evening, at 8.15 o'clock, the Society met in Joint Session with the New York Section of the American Chemical Society, Prof. Chas. Baskerville occupying the Chair. A short address was made by Dr. Chas. F. McKenna upon the "Care of Explosives in Large Cities," after which President Walker delivered his Presidential Address, which will be found printed in full in these Transactions.

Dr. H. E. Patten, of the Bureau of Soils, Department of Agriculture, then lectured upon "Surface Tension and Its Relation to Electrochemical Action," also printed in these Transactions.

PROCEEDINGS OF SATURDAY, APRIL 8th.

The meeting was called to order by President Walker, in the Rumford Auditorium, at 10.00 A. M.

Papers by Jas. Lyman, Chas. G. Osborne, John W. Beckman, A. E. Greene, Carl Hering, F. P. H. Knight and Chas. Vey Holman were presented and discussed as printed in full in these Transactions.

The Secretary presented the following resolution, which was numerously seconded and unanimously passed:

Resolved, That the sincere and hearty thanks of the American Electrochemical Society be extended to the following persons, organizations and firms, for their voluntary and much-valued co-operation in the Nineteenth General Meeting of this Society:

The Chemists' Club,
The New York Section of the American Chemical Society,
The Nichols Copper Company,
The Hanson and Van Winkle Company,
Dr. F. J. Maywald,
The Moss Engraving Company,
The New York Electrical Testing Laboratories,
The College of the City of New York,
Columbia University,
The American Smelting and Refining Company,
The Local Committee in charge of the Meeting, and, in particular, The Ladies' Committee.

President Walker then declared the Nineteenth General Meeting of the Society adjourned.

In the afternoon a party of over 100 members and guests visited the Perth Amboy plant of the American Smelting and Refining Company, at Maurer, N. J., spending three hours in a highly instructive and interesting inspection of the plant, under the leadership of Mr. W. S. Morse and a dozen of the working staff of the plant.

This Perth Amboy plant comprises ore smelters, lead refining plant, electrolytic copper refining, electrolytic silver refining and the Bessemerizing of leady copper mattes in basic-lined converters.

This immense plant refines, per month, 7,500 tons of copper, 8,000 tons of lead, 3,000,000 ounces of silver and 20,000 ounces of gold. In doing this, it smelts 15,000 tons of ore and Bessemerizes 1,500 tons of leady copper matte. The attention of members was particularly attracted to the basic-lined converters, the latest improvement in the metallurgy of copper.

In the evening the New York Section of this Society tendered an invitation smoker in the rooms of the Chemists' Club to the visiting members and guests of the Society and to the members of the Chemists' Club. Several hours were passed in social intercourse and relaxation (bordering, perhaps, upon hilarity), thus closing the most successful meeting of the Society yet held in New York City.

Entertainment of Ladies.

A small but active Ladies' Committee arranged some very enjoyable entertainments for the visiting out-of-town ladies, who numbered nearly a score.

On Thursday afternoon a drive was taken through Central Park and the Riverside Drive, ending with tea at the new Plaza Hotel.

On Friday afternoon the Metropolitan Art Galleries were visited.

On Saturday afternoon the establishment of Tiffany and Company, including their Art Galleries, was visited, and the Museum of Natural History.

On Saturday evening the ladies occupied a box at a theater party.

ANNUAL REPORT OF THE BOARD OF DIRECTORS

To the Members of the American Electrochemical Society:

We submit herewith the annual report of the Secretary and the Treasurer for the year 1910, the former containing the detailed financial statement of receipts and expenditures.

The increase in the number of members was very satisfactory, being 145 net during the year. The active work of the Membership Committee bore its usual good fruit during the year. The membership at date of this meeting is, in round numbers, 1,270, with 54 members elected but not qualified by payment of dues, so that the number of members at this date is practically 1,324.

The financial status of the Society during 1910 was also satisfactory. The excess of receipts above expenditures for the year was $1,176.40, from which the permanent investment fund was increased by the purchase of another $1,000 5 per cent. interest-bearing bond. The equity of the Society in the four $1,000 bonds held at the close of 1910 (diminished by the $500 Ferro-boron prize, held in trust) was over $3,500.

The following are the more important actions taken by the Board of Directors during the past year:

The recommendation of Dr. A. E. Kennelly was adopted, to the effect that wherever English measurements are mentioned in our Transactions, the metric equivalents be given.

A Local Section of the Society in Chicago was authorized upon the petition of Mr. A. B. Marvin and eleven other members of the Society.

The sum of Fifty Dollars was appropriated to Prof. W. D. Bancroft, Chairman, for the uses of the International Committee on Units, appointed at the last International Congress of Applied Chemistry.

Prof. W. S. Landis was appointed Assistant Secretary of the Society.

The usefulness and influence of our Society continue their rapid extension, and its progress and success are such as to make us believe that we may well be considered a model Scientific Society of international scope and activity.

WM. H. WALKER, *President.*
J. W. RICHARDS, *Secretary.*

SECRETARY'S ANNUAL REPORT

To the Board of Directors of the American Electrochemical Society:

GENTLEMEN:—In 1910 the Society held two General Meetings, one in Pittsburgh, Pa., May 4th, 5th, 6th and 7th, at which the attendance was 192 members and 253 guests; total, 445—the largest recorded attendance at any meeting of the Society; the second in Chicago, October 13th, 14th and 15th, at which the attendance was 112 members and 114 guests; total, 226. The latter was the first meeting of the Society in Chicago, at the invitation of the newly-formed Chicago Section, and undoubtedly strengthened very much the opportunities for usefulness of the new Section in that locality. At the Spring Meeting, 27 papers were read; at the Autumn Meeting, 23.

In 1910 there were issued and distributed to our members two Volumes of our Transactions—Volume XVI, the Transactions of the New York City Meeting of October 28-30, 1909; Volume XVII, of the Pittsburgh Meeting of May 4-7. These Volumes contained 480 and 431 pages, respectively.

The Transactions of the Chicago Meeting of October 13-15, 1910, were issued as Volume XVIII on January 25, 1911; it contained 293 pages.

The edition of each of the 1910 Volumes was 1,500 copies, bound in cloth, for distribution to our members; 50 extra copies in sheets for distribution in pamphlet form to authors of papers; 250 copies, bound in paper, for distribution to the Faraday Society, and 500 copies, sewed, ready for binding, to be kept in stock.

In the 18 Volumes now issued as the Transactions of the first nine years' activity of the Society there are 453 communications, covering 6,424 pages.

Complete sets of these Transactions are still on hand, but the stock is diminishing rapidly, and Volume 3, which is nearly exhausted, is sold, according to the action of the Board of Directors, at double price.

A pamphlet containing the Tables of Contents of the first 18 Volumes has been printed and distributed to all members and purchasers of the Transactions. It is intended to issue, in 1912, an Alphabetical Index of the contents of the first 20

Volumes of the Society's Transactions, which will undoubtedly increase considerably to members the value of their Transactions as a working Electrochemical Library.

The stock of Volumes on hand December 31, 1910, was as follows:

Volume	Bound in cloth	Bound in paper or stitched ready for binding	Total
I	250	10	260
II	233	0	233
III	158	0	158
IV	189	234	423
V	130	234	364
VI	146	239	385
VII	149	247	396
VIII	151	237	388
IX	164	271	435
X	174	257	431
XI	168	261	429
XII	177	266	443
XIII	174	220	394
XIV	263	253	516
XV	30	502	532
XVI	80	521	601
XVII	278	517	795
Total			7,183

Condition of the Society in regard to Membership in 1910:

Members January 1, 1910		1,066
Elected and qualified as members in 1910		183
		1,249
Resignations in 1910	19	
Deaths	6	
Dropped for non-payment of dues	13	
	—	38
Members December 31, 1910		1,211
Net gain in membership in 1910		145

Financial Statement.

January 1, 1910 to December 31, 1910.

RECEIPTS.

Entrance fees		$ 870 00
Current dues		6,221 31
Sales of publications		1,253 90
Membership certificates		28 00
Advertising		261 10
Interest on investments and bank deposits		221 49
Donation, Pittsburgh section		204 94
Temporary loan, November-December		250 00
		$ 9,310 74

DISBURSEMENTS.

Office printing		$ 433 80
Postage		1,150 00
Publications		3,749 59
Office expenses		344 00
Storage and packing		26 38
Salaries		946 92
Expenses of Meetings		387 55
Appropriations to sections		50 00
Appropriation to Committee on International Standards		50 00
Faraday transactions, payment for extra copies		263 34
Membership committee, appropriations		457 50
Engrossing membership certificates		9 60
Commissions paid on advertisements		15 46
Repayment of temporary loan		250 00
Permanent investment		1,049 86
Increase of cash balance on hand		126 54
		9,310 74

ASSETS, JANUARY 1, 1910.

Cash balance, January 1, 1910, on deposit		$ 840 59
Cash box		50 00
Bonds held by the Society (cost price)	$2,998 75	
Ferro-Boron prize, held in trust	500 00	
Equity of Society in above bonds		2,498 75
		$3,389 34

ASSETS, DECEMBER 31, 1910.

Cash balance, December 31, 1910, on deposit		967 13
Cash box		50 00
Bonds held by the Society (cost price)	$4,048 61	
Ferro-Boron prize, held in trust	500 00	
Equity in Society in above bonds		3,548 61
		$4,565 74
Gain in assets for the year of 1910		1,176 40

The Society continues to prosper financially, scientifically and socially, and speaking as Secretary, I have nothing further to recommend than the continuation of our present liberal and progressive policy.

Jos. W. Richards,
Secretary.

TREASURER'S ANNUAL REPORT

FOR THE YEAR 1910.

Balance January 1, 1910		$ 890 59
Receipts from Jos. W. Richards, January 1, to December 31, 1910		9,310 74
		$10,201 33
Payments January 1, 1910, to December 31, 1910, as per list		9,184 50
Balance December 31, 1910		$ 1,017 13

Pedro G. Salom,
Treasurer.

We the undersigned have examined and compared the receipts and expenditures of the American Electrochemical Society, and find the same to be correct.

(Signed) Henry G. Morris,
S. S. Sadtler,
Auditors.

MEMBERS AND GUESTS REGISTERED AT THE NINETEENTH GENERAL MEETING

Members.

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Chas. E. Acker	John T. Baker	Edw. R. Berry
G. Alleman	W. D. Bancroft	Joseph Bijur
R. Amberg	Chas. Baskerville	W. F. Bleecker
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Miss C. Taylor
Mrs. M. Toch
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Mrs. D. Wesson
Miss M. O. Wesson

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D. D. Berolzheimer
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P. K. Devers
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B. G. Fernberg
A. Finck
T. Fukui
F. W. Garen
S. H. Graham
J. Griffin
J. H. Hall
W. A. Hamor
D. S. Hartshorn
W. A. Hendryx
B. C. Hesse
R. Hewitt
A. E. Hikelman
F. Holmgren
E. B. Jewett
R. Kann

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T. L. B. Lyster
P. Luhr
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J. H. Mathews
I. C. Matthews
J. H. McCreary
F. C. Meucke
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G. D. Morgans
A. Neisch
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C. H. Von Baur
F. S. Wayne
C. Y. Wen
M. C. Whitaker
D. L. Williams
K. Wooyenaka
D. K. Wright

Members Elected and Qualified.

December, 1910—April, 1911.

December 31, 1910.

Albert C. F. Hiorth, Christiania, Norway.
Lars Yngstrom, Falun, Sweden.
Anders Borgen, Jossingfjord, Sogndal i. Dalene, Norway.
Edgar E. Arison, Chicago, Ill.
Dr. Louis Schaefer, Maywood, N. J.
Geo. L. Tifft, Wauwatosa, Wis.
Frederick L. Theurer, Madison, Wis.

January 28, 1911.

A. W. Kruemmer, New York City.
J. Vincent Hunter, Fort Wayne, Ind.
Emilio Romanelli, State College, Pa.
Irving W. Wilson, Boston, Mass.
Otis Hutchins, Boston, Mass.
Albert Ray White, Madison, Wis.
Hans Mannhardt, Chicago, Ill.
Philip J. Lonergan, Denver, Col.
Ray Potter Perry, Cleveland, Ohio.
Bradley Dewey, Pittsburgh, Pa.
Harry H. Bates, Joliet, Ill.
Palmer H. Langdon, New York City.
Morton Liebschutz, Newark, N. J.
Edmund G. Spilsbury, New York City.
Gellert Alleman, Swarthmore, Pa.
Edward B. Shimer, Easton, Pa.

February 25, 1911.

Louis W. Adams, South Bethlehem, Pa.
Chas. W. Hill, Cleveland, Ohio.
Lewis B. Lindemuth, Steelton, Pa.

Members Elected and Qualified (Continued).

J. J. Dunn, Ellwood City, Pa.
Henry M. Hall, Massena, N. Y.
George B. Hogaboom, Newark, N. J.
Haakon Styri, Christiania, Norway.
Oliver W. Storey, Ambridge, Pa.
Lindsley Loring, Westwood, Mass.
Dr. Paul Askenasy, Karlsruhe i. B., Germany.
Geo. A. Hopkins, Munhall, Pa.
John J. Nolan, Dollar Bay, Mich.
Geo. I. Kemmerer, Socorro, N. M.
Fay Woodmansee, Maywood, Ill.
Frank P. H. Knight, Keokuk, Iowa.
Thaddeus F. Baily, Alliance, Ohio.
Willett H. Barton, Goldfield, Nev.
Dr. Edward Sokal, Chicago, Ill.
J. C. Parkinson, Massena, N. Y.
Chas. N. Waite, Wilmington, Del.
Orrie C. Kelley, State College, Pa.
Joseph Langsdorff, New York City.
Paul H. Mayer, Mt. Vernon, N. Y.
Chas. E. Pope, Pittsburgh, Pa.
Wm. M. Snow, Peru, Ill.
Frank R. Kemmer, Massena, N. Y.
Harrington Emerson, New York City.
Walter W. Ziegler, Fremont, Ohio.
Chas. Vey Holman, Bangor, Me.
Edwin R. Leach, San Francisco, Cal.
E. B. Bragg, Evanston, Ill.
Wm. Wallace Murray, Baltimore, Md.
Henry Hess, Philadelphia, Pa.
E. R. Smithrim, Sault Ste. Marie, Ont., Canada.
Robert H. Bradford, Salt Lake City, Utah.
Wm. A. Slater, Port Arthur, Texas.
Chas. Darwin Test, Golden, Col.
Arthur J. White, Philadelphia, Pa.
James Roger Crocker, New York City.

April 6, 1911.

W. S. Andrews, Schenectady, N. Y.
Francis P. Dunnington, University, Va.
G. Wm. Bjoerkstedt, Indiana Harbor, Ind.
Max Lemberg, Sewaren, N. J.
Linwood T. Richardson, Madison, Wis.
Elwood A. Richardson, Madison, Wis.
M. Appel, South Bethlehem, Pa.
Dr. Bruno Fels, Charlottenburg, Germany.
Francis C. Nicholas, New York City.
Anthony F. Lucas, Washington, D. C.
James H. Gray, New York City.
Chester A. Walter, State College, Pa.
Corydon P. Karr, Plainfield, N. J.
Avery H. Reed, Rosiclare, Ill.
Moses M. Riglander, New York City.
Alfred Schwarz, Lancaster, Pa.
Gustave P. Metz, Newark, N. J.
Dr. Abraham Tessler, Newark, N. J.
Chester H. Thordarson, Chicago, Ill.
Abel H. Hamblet, Rumford, Maine.
Robert J. Weitlaner, Buffalo, N. Y.
Clarence H. Ohlwiler, Altoona, Pa.
Geo. W. Haering, Terryville, Conn.
Wm. H. Peirce, Baltimore, Md.

The Presidential Address, delivered at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 7, 1911. Professor Chas. Baskerville in the Chair.

CHEMICAL RESEARCH AND INDUSTRIAL PROGRESS.

By Wm. H. Walker.

Within the last few years research has become a word to conjure with. Webster defines it as "diligent inquiry in seeking facts or principles; continuous search after truth." To find the truth is, therefore, the keynote of research. But although the great activity in research which so marks the present is essentially modern, an inquiry after truth is surely not new. The human mind has from the gray dawn of antiquity longed for and sought after truth. The new field of human endeavor epitomized by the word research, represents a change in the method of finding truth rather than in the intensity of desire to know the truth. When a great thinker of the past wished to investigate a subject he simply sat down in a quiet nook or walked through academic groves and philosophically meditated concerning it. He believed that he could know things as they are and had great faith in the accuracy of his conclusions. As a mental performance such philosophical labor was not altogether without value, but since we cannot know things as they are, but must know them as they appear or manifest themselves, a search for truth can reach its goal only through intimate contact with the things themselves and an accurate determination of the facts concerning them.

At the time when the followers of Aristotle were speculating upon the constituent parts of the universe, and concluding that everything was composed of fire, water, air and earth, with the material transformations which each could undergo, there were other men who were devoting their attention to the real transformation which materials do undergo. These people had glass, a product showing a marked change when compared to the raw materials going into its production; they were able to dye the royal purples and to bleach the fine linens. They had the knowl-

edge to smelt iron and copper, tin and lead from their ores—surely striking transformations which they could actually see. But the truth concerning these phenomena did not interest the men the achievements of whom history has seen fit to chronicle. The dictum of Aristotle that "industrial work tends to lower the standard of thought" prevailed, and it is to this want of sympathy that we must ascribe the fact that the old historians failed to note the discovery of even the most important chemical processes, while they gave detailed accounts of those men who advanced mere speculations and taught untenable opinions on the constitution of the universe.

But groping in the utter darkness of these early times, the men who actually did things in the utilization of natural phenomena in contradistinction to their more famous brethren who only talked and idly speculated about them, were the real pioneers in chemical research. Their quest for truth was however so crude, and their endeavors so little appreciated, that almost no real progress was made. The teachings of the philosophers that there was required but the *"quinta essentia"* in order to transform one of their four elements into another, together with accidental observations on the part of some pseudo-scientists, led to that studied attempt to transmute the baser metals into gold, which lasted for many centuries. If but the "Philosopher's Stone" could be found, the problem would be solved. This was the goal of the alchemists. It would be a perversion to describe the labors of these men as a search for truth; their objective point was gold, not truth, and many a devoted life was spent in this fruitless quest.

It may seem a long step from the work of the alchemists with all their magic and mysticism, their sordid lives and their cherished secrets, to the consideration of the intense human activity of the present day with those gigantic undertakings and marvelous achievements collectively called modern industry. But there may be something in common between the work of the ancient investigators and their influence on civilization, and chemical research of to-day and industrial progress.

The course of human events has been compared to a pendulum. We tend to swing to extremes—to go too far first in one direction and then in the other, when real progress lies in the middle. The

period of alchemy represents the pursuit of science for selfish and mercenary ends; they cared for nothing but to be able to make gold. The pendulum was at an extreme end of its path. Nor did they make material progress in their methods. The alchemists of Arabia and early Germany were little wiser than their predecessors of Egypt who flourished many centuries before them. The explanation of this lack of progress is to be seen in the profound secrecy which they at all times maintained. When some enterprising worthy did take it upon himself to transcribe for future generations his knowledge of the mystic art, his sentences were so ambiguous and his diction so involved as to make the whole entirely meaningless. They even employed mysterious symbols to render the more difficult any attempt at imitation.

There was therefore, no acumulation of knowledge or experience, and each succeeding investigator continued to grope around in the darkness which had ever enveloped his calling, without deriving any benefit from the labor of either his predecessors or his contemporaries. The great and insurmountable obstacle to progress was nothing more than the jealous secrecy engendered by selfish competition. Both confidence and co-operation were entirely wanting. Each one feared that his neighbor might profit by his experience were it to become known, never realizing that he must in the end get much more in return than he gave. There was but one of him, while there were many of his neighbors.

But in the thirteenth century there came a change. One Roger Bacon, who from his rare accomplishments and erudition was called "Doctor Mirabilis," and who firmly believed in the existence of the philosopher's stone, was being tried at Oxford for sorcery. To disprove the charges against himself, he wrote a celebrated treatise with a long Latin name, in which he showed that phenomena which had been attributed to supernatural agencies, were in fact due to common and natural causes. He pointed out further, in his brief, a possible distinction between what he called theoretical alchemy, or work which would advance the knowledge of natural phenomena, and practical alchemy, or the striving after immediately useable information. He is to be regarded as the intellectual originator of experimental research,

and by his generous treatment of the knowledge gained gave to science the impetus for which it had so long waited. The limitations of this paper preclude my following in any detail the development of chemistry through the succeeding centuries, but it can be easily shown that just as knowledge was sought after for its own sake, and in proportion as there was free and honest intercourse among the investigators of the time, just so rapidly was real progress made.

With the appearance of men who took an absorbing interest in the study of natural phenomena for the purpose of gaining a deeper insight into the world around them, when investigations were undertaken from a desire to know, and to acquire knowledge which could become the property of the world at large, the pendulum began to move back.

For years the efforts of investigating minds were devoted to the explanation of the phenomena of nature, to the discovery of new laws and principles, to the accumulation and organization of facts into what is called a "Science"—to a real search for truth. This resulted in a general uplift of humanity, an advance in civilization which cannot be described or measured in words. This was a time when the human mind was struggling to determine realities in the midst of tradition and superstition, to realize that nature is always complex but never mysterious and that dependence should be placed on proven facts rather than in the vagaries of priests and philosophers. Then man became intellectually free.

But for many years after the broad generalizations upon which modern chemistry is founded were well established, industry did not profit much by scientific work. One hundred years ago the men who smelted iron and copper, lead and zinc, knew little of the principles underlying their practice. Leather was tanned, woolens, cottons and silks dyed, porcelain and glass were made, without the aid of those who alone knew the chemistry involved. I do not mean that scientific men took no interest in the manufacturing industries, for we can recall the great work of Liebig for agriculture, and the immense amount of analytical chemistry which is the foundation of industrial chemical practice; but these were times when the advance in chemical knowledge was far ahead of the development of the industries on the success of

which our material comforts depend. The pendulum had swung to the other extreme.

A rational attempt to apply chemical knowledge and methods commenced about 1850. It was in 1856 that Perkin made the first synthesis of a coal tar color, and founded the industry which has become the most remarkable example of applied chemistry that we have. In 1855 Bessemer introduced his revolutionary process for making steel, made possible by the clear understanding of the nature of steel through improved analytical processes.

Up to this time, when a man became a student of chemistry it was because of the attractions which he found in scientific study, because of his "delirious but divine desire to know." On the other hand, a man who intended to devote his life to the carrying on of some industry did not study chemistry at all, or if he did, it was in a superficial and most perfunctory way. With the establishment of great technical schools there was produced a class of men who, notwithstanding the fact that they intended to follow industrial work as a career, studied chemistry in such a way as to become masters of the fundamental principles underlying the science, as well as possessors of a great mass of scientific knowledge and experience. Possibly more important even than this, they became imbued with the scientific method of thought and work. Such men carried science into the industries and applied to the solution of the practical problems of the day the knowledge of chemistry which was theirs. Hence the last fifty years may be said to be characterized by the production of men who combine the ability to appreciate and enjoy work in science for itself alone, and who also possess the ability and inclination to apply their chemical knowledge and training and to make the results of the work of past generations of pure scientists of ever increasing service to humanity.

But within the last ten or fifteen years we have seen a third kind of chemical activity develop, namely a class of men who, while possessed of the ability and love of science which characterized the leaders in pure science of old, yet are not handicapped by the doctrine of Aristotle, that contact with industry contaminates thought. This movement is seen in the tendency of great industrial organizations to establish research laboratories within themselves, and in the willingness of educational institu-

tions to maintain research work in those fields of chemistry which are immediately applicable to industrial practice.

For the purpose of further studying the relationship existing between chemical research and industrial progress, we may therefore divide this kind of chemical activity into three classes. First, we have that which for want of a better term we will call original work in pure chemistry; second, we must consider the work of the so-called industrial chemist, the man who primarily applies existing chemical knowledge to the accomplishment of specific ends; and third, we have research work in what again for want of a better name we will call applied chemistry.

It is but a truism to say that there is no more dignified, honorable, or altogether delightful calling in life than the pursuit of science for her own sake. The biographies of the great altruists of science are ever an inspiration to the student of human progress. The man who devotes his life to the accumulation and dissemination of knowledge without thought of return other than the gratification incident to discovering nature's secrets and adding to the sum of the world's knowledge, is living in many respects an ideal existence. But such men must subsist, and if the results of their work bring no financial return they must have some vocation for which the world is willing to ensure payment. Thus it comes about that for the most part our educational institutions have been the source from which such work has sprung. The environment of pure science has in the past been academic, its home has been in the schools of learning; the great investigators were teachers. Of course there are exceptions, but the honor roll of science is essentially an academic list. This is true in America as in Europe, and yet there is a very different attitude shown towards men of science and their work by the manufacturing public here and in Germany, for example. There, the dictum of the University carries authority, while our feeling is shown rather clearly by the somewhat sarcastic tone with which we use the word *academic*. It is usually a term of mild contempt, and is used synonymously with impractical, unworkable, connoting a lack of acquaintance with cold facts. That great scientist, Professor William Östwald, when addressing the Liverpool Section of the Society of Chemical Industry on the causes of the great success of the German chemical industries, said in sub-

stance: "We might sum up the facts by saying that Germany managed to put more brains into her goods, or if we prefer a more scientific expression, to combine more mental energy with the rough energies of primary material. There is no doubt that the English store of mental energy is as great as that of Germany, the only difference being that the channels leading that energy into industries are not so broad or deep or numerous as in Germany. There seems to exist in parts of Great Britain not only a disregard for, but even a mistrust of science or theory. In Germany everybody trusts science, even the Government. They are quite accustomed to consult a scientific expert before going into a new business. Of course there have been cases in which they failed to act in this way, but then they generally fell into scrapes. Sometimes even theory led into scrapes; but it proved to be bad or incomplete theory. But the sum total of experience has convinced them of the value of theory, and their trust in it is rather too large than small."

This statement does not apply alone to England. Our American industries have flourished very well, it is true, but rather in spite of a lack of scientific aid than on account of such aid. This high regard with which science is held by even the less educated manufacturers of Germany, while undoubtedly the true basis of the splendid achievements resulting from the co-operation of science and industry, is probably not to be realized in America in the immediate present. High respect for science is a characteristic of the German, and is possibly a result of years of military discipline as a part of a monarchical government. Can it be true that the spirit of freedom has run so riot in America that we have come to believe that we are not subject even to the laws of nature? Supplied with bountiful resources far beyond what any other nation enjoys, protected by a tariff wall higher and tighter than those of our commercial competitors, we have grown vastly satisfied with our own achievements. To quote from a keenly observant contemporary: [1]"We marvel at our enterprise in scraping iron ores from the earth's surface by steam shovels, in growing wheat on virgin soil, in stripping great areas of primeval forests, in burning natural gas, and allowing petroleum to spout from the ground. Even Germany acknowledges that

[1] Arthur D. Little, in "A Laboratory for Public Service."

she cannot compete with us in raising cotton, and we cut more ice in a month in the single State of Maine than all the Pictet machines in France can turn out in a year. We control the copper market of the world because we have the copper. If cheap sulphur is wanted, we pump it from the ground. We develop great centers of power distribution, because our rivers run so fast down hill. To these vast resources we have, indeed, brought a native energy, an unusual capacity for organization, and a genius for mechanical affairs. What we do we do on a large scale, but we often do it very badly. It is quite time for us to pause in our self congratulation long enough to inquire whether the things we are doing cannot be better done, whether in fact other nations have not developed and put to use much better methods, which, given an equal opportunity, put our performance to the blush."

There is thus a mutual obligation existing between our educational institutions and our industries. The former must continue to increase their facilities for that research which has made the German Universities the avenues through which German civilization and industry have been brought to the point that we find them to-day.

On the other hand, the industries should not fail to recognize that progress based alone on industrial prosperity is but apparent progress, and that a sound civilization depends not only on conditions which make for material comfort, but on the culture which comes from an education in the broad sense that scientific research implies.

The great tendency of our times is towards service. This is seen in every sphere of human activity. The philosophy of even one hundred years ago was largely speculative; while doubtless mentally invigorating, it did not in the last analysis contribute toward that progress which alone makes life worth the living. As a result, all past systems of philosophy have been thrown back into the realm of literature or of poetry. The trend of modern philosophy is toward a study and realization of things as they manifest themselves, and not a mere guess at what things probably are. In religion too we note a change. There was a time when the main object of one's religion was to save one's own soul, without much regard to the souls of others. But we no

longer recognize particular virtue in shutting one's self up within heavy walls, in order to render one's life more pure by reason of lack of contact with the great mass of humanity. We no longer admire the self sacrifice of the immured monks of Thibet —we simply pity them. Religion is to-day rather the great inner consciousness, which renders one's own future condition secure by aiding the present condition of others. The great religions of to-day make for righteousness—through service.

In the same way there is with scientific men a general awakening to the fact that the highest destiny of science is not to accumulate the truths of nature in a form that no one but the elect few can utilize, but that the search for truth can be combined with a judicious attempt to make the truth serve the public good. Thus the distinction which has existed between the terms pure science and applied science is rapidly falling away. An attempt to define these two kinds of science reveals the fact that this distinction is a general impression rather than a clear statement. A fundamental law of psychology is that thought tends to pass over into action. Applied science is nothing more than the realization of this, and is thought in action. Force does work only when in motion—so are ideas of value only when carried into effect.

But the carrying of an idea into practice is not always an easy matter. It is frequently much easier to make a discovery or to develop a new fact than it is to make of such a discovery a serviceable reality. For example, the reactions underlying the ammonia-soda process were well known as scientific facts for many years, but this knowledge did not benefit the world until the genius of Solvay made through it purer and cheaper soda available. Cavendish long ago discovered that an electric spark produced nitric acid in the air; the world waited until but a few years ago in order to profit by this knowledge. It was then that the researches of Birkeland and Eyde made of the idea an industrial process.

Many facts like this last were known which did not materially influence the industries of the times because there was necessary a knowledge of how to obtain and apply large quantities of electrical energy. Thus Wöhler discovered the reaction by which phosphorus could be readily distilled from a mixture of bone

ash, sand and coke; but it remained for Readman and Parker to apply internal heating by electrical means to thus make phosphorus. Wöhler also discovered calcium carbide and its property of yielding acetylene. The beautiful light from this source was not made possible, however, until the development of high-powered electric generators made its cheap production an easy matter. Men who can interpret the scientific results already available have been of incalculable value in the growth of our industries, and there will ever be a field for this type of chemical activity. In fact it is just here that we find the 'faith in science' of the Germans, of which I have spoken, bearing fruit. In America there is a national lag in the application of new scientific data to every-day problems. We, as a people, are so wonderfully keen in developing mechanical ideas when once they are presented, that the marked lag in the acceptance and application of chemical principles is the more remarkable. The industries themselves are frequently to blame for disappointing results which sometimes are met in an attempt to introduce scientific methods into their works. They employ a so-called chemist, without inquiry as to whether he has had the kind of training that could be expected to fit him for the work he is to do. They furnish him with a meagre equipment and then expect revolutionary results. When these are not forthcoming they exclaim in disgust, "There is no money in chemical control, or in chemical research; we have tried it." It is just as though I should decide to increase my income by adding to my other activities that of horse-racing. I buy a well-meaning but untrained horse, and enter him for the race. He fails to win the purse, and I exclaim "There is no money in horse-racing; I've tried it." Or probably my analogy would be more complete if I would suppose that I bought a well-trained, capable horse, and then hitched him to a coal-wagon or an ice cart, and started him off. Then because he fails to win out over the horses in racing sulkies, I again affirm, "No, there is no money in horse-racing; I've tried it."

While it is true that the manufacturing industries as a whole have been slow in accepting the aid of science, and while the American public lack such belief in the part which science plays in the advance of the world as is possessed by some other nations, there is a distinct and most promising movement under way which

will have a marked effect upon our industrial progress. This is the impatience shown by some of the more enterprising manufacturing concerns to wait for scientific facts to be discovered by others, and their willingness to establish research laboratories within their own organizations—to actively enter the field of research in applied chemistry.

From what has already been said, there may appear to be a paradox hidden in the expression 'Research in Applied Chemistry.' How can the element of research enter into the work of applying to definite ends the facts already established as true by others? Is there a difference between research in so-called pure chemistry, and research in what, for want of a better name, we will call applied chemistry? Possibly I can make the distinction clear by a rough analogy. The development of research in a science may be compared to the exploration of a new country. New roads are to be laid out, tunnels bored, and bridges built; in other words, new problems solved. This may be done in two ways. First, constructive work may be undertaken wherever an interesting problem presents itself, without regard as to whether there is a demand for such a structure or not. It is built because of the interest of the builder in solving this particular difficulty, and the pleasure he takes in it, knowing also that sometime it will be utilized. As a rule he is under no great pressure to get the structure completed. This may represent the method of pure chemistry, and the great advance in chemical knowledge of the past was made almost entirely by boring just such tunnels, and building just such bridges. The industries have used these structures when they could, or when some second builder could adapt them to use. Research in applied chemistry differs from that just described only in this, or I should say it *needs* differ only in this: that when a problem is to be solved, a bridge to be built, the work is undertaken at a point where there is a demand for its use, where people are waiting to cross over as soon as it is finished. The method of building is no different, the difficulties no less. The fact that the bridge is to be used makes the work of building no less dignified, nor is it carried out with less pleasure. In both cases the builder profits by all that has been done before, and contributes his bridge, together with the new materials of construction which he may have found,

to those who may come after him. To cite an example from experience, suppose I were to determine the electrical conductivity of metallic oxides at high temperatures, with great accuracy, and publish the results, without reference to any particular application of the data. This is pure science. But suppose I am trying to perfect an electrical heating unit for high temperatures and, in insulating my resistor, I do this identical piece of work, namely, measure with great accuracy the electrical conductivity of metallic oxides at high temperatures, and again publish the results. This is applied science. The work need not differ in the least degree. It can be as accurately done in one case as the other, and the conclusions as scientifically drawn. The mere fact that the data will be used for some practical end need not make the investigation any less scientific.

Why is there not then the respect for this kind of work, as when a bridge is built with the knowledge that it may not be used for an indefinite period? Why then does an eminent writer a few months ago lament the fact that there is not more research "uncontaminated with worship of usefulness?" Why does usefulness contaminate? I think it lies in this: The investigator of pure science works in the broad daylight, throws his product open for inspection, and invites all to come and use it when they can. In applied chemical research the spirit of the alchemist tends to creep in. The builder keeps his materials of construction and his designs a secret, and so boards up his bridge that those who cross over it cannot see how it was built or profit by his experience. The moment a thing becomes useful we become jealous of its possession, we become narrow in our horizon; we sell our scientific birthright for a mess of pottage—we become alchemists.

There is a heavy moral obligation on the part of large industrial organizations having fully equipped research laboratories, to contribute their share to the advance of the world's knowledge. An obligation to see to it that they do not become saturated with the spirit of alchemy. They have well stocked libraries, and are provided with all the current periodicals; they profit by all the scientific work which has been done and is being done. This is as it should be, and such firms are to be commended for their progressiveness. But is this not a reason why such laboratories

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should do their part in adding to the sum of available knowledge? There is in every laboratory much work which could be published, and yet conserve the interests of the corporation. First there are the results which may not have proved valuable to the laboratory in which they were obtained, but which would be of immense value to someone else working in an entirely different field. Second, there are those results of value to the laboratory possessing them, but which could be published in an un-applied or 'pure' form, and which would make an important contribution to science and at the same time the publication would work no injury to the company or the corporation most interested. And finally there are those results of operations and processes, machines and apparatus, which, if the truth were known, are possessed by a number of concerns, but are held as valuable secrets by each. Everyone would profit and no one be the loser by so far-sighted and generous a policy. Germany is very justly held up as a shining example of marvelous industrial progress and prosperity. A very great deal of the credit for her present position is due to her splendid educational system. But no small factor in her national progress is the helpful attitude which her industrial organizations take toward the publication of scientific data. The individual does not suffer, while Germany both from a purely scientific and an industrial standpoint is rapidly advanced. But too often with us, the President and his Board of Directors are alchemists; they fail to see why if they pay the salaries of the research men, they should give to the public, or their competitors, any part of their results. They exclaim: "What has posterity done for us?" They would have their laboratories remain the secret chambers of the alchemists, and continue to improve their methods of changing baser materials into gold, without regard to the obligations which they owe their fellows.

It is to the men who form the working force in our industrial laboratories that we must in a great measure look for making our national scientific societies the power for industrial progress which they ought to be. But it is this general disinclination on the part of industrial concerns to allow their chemists to disclose in any measure the results of their work by contributing papers for the meetings, or in entering heartily into the discussions, that makes this realization difficult. This is to be deeply lamented,

and we believe it is a fundamental mistake; a short-sighted policy which can but react upon industrial progress as a whole. We cannot operate a scientific laboratory as we would a factory. The conditions of maximum productiveness are not found in an atmosphere of selfish rivalry. An English writer of broad technical experience has said, when speaking of the cry for technical education, [2]"Until the nation as a whole recognizes that the prosecution of scientific study as a mere means of money making is a profanation defeating its own ends, the history of the industrial development of England will afford the same melancholy spectacle in this as in the last century, technical education notwithstanding." All attempts at machine-made scientific results are doomed in the long run to failure. They compare with the achievements of men working under conditions of mutual helpfulness as does a machine-made Nottingham curtain to the beautiful hand-made lace of the French convents.

It requires no extensive mathematical calculation to prove that the manufacturers themselves would be the ones to profit by such a liberal treatment of the results of scientific work. Of one hundred manufacturing concerns, each one would give but one percent of the whole contribution, while he would receive the remaining ninety-nine percent. He could not in the long run be the loser. But of vastly more importance, he would feel and know that his organization was taking part in a world movement toward that increase of human knowledge upon which all real progress depends. The greater sense of satisfaction, the greater success even of an industrial organization, lies in a fuller, freer, more generous publication of the scientific results of their laboratories.

Would that we might benefit by the experience of Solomon, King of Israel, who, when asked "What shall I give unto thee," replied, "Give me knowledge and wisdom;" and he was answered, "Wisdom and knowledge are granted unto thee, and I will give thee riches and wealth and honor."

[2] Dr. Carl Otto Weber. The Chemistry of India Rubber.

A paper presented at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 6, 1911, President Wm. H. Walker in the Chair.

DRY CELL TESTING.

By W. B. Pritz.

There are today at least 100 brands of dry cells upon the market, varying in quality from very efficient and reliable cells to those which must be considered very inefficient; and from these the consumer must select that brand which in his opinion will give best service. Before any conclusion can be reached regarding the adaptability of a cell to a particular service, the consumer must either accept the guarantee of the manufacturer or make for himself, as best he may, a service comparison of the cells in question.

Non-Uniformity in Dry Cell Testing.

The need, then, for trustworthy and comparable methods of testing becomes very plain. Certain tests have been instituted, the chief feature of which, until recently, has been that the method requires a short period of time for completion, a condition which, in the earlier years of the industry, was entirely justified by the very rapid improvements made upon the product. One of the earlier tests of this nature consisted of a continuous discharge thru 2 ohms until the working voltage fell to a certain fixed value, a resistance much lower than is usually employed in connection with cells. It was not long, however, before it was realized that results obtained by this method of testing were not comparable to results obtained in actual service, and we note with satisfaction that these short-lived, heavy-drain tests have been largely replaced by tests the conditions of which are intended to be as nearly as possible those of actual average service.

There is another factor which is in part responsible for the many diversified tests which may be found in texts, trade publications, etc. The many uses to which dry cells are put and the vast differences in operating conditions have brought forth, on the part of the larger consumer, tests related in some manner to the

service in which the cells are to be used. No doubt such tests are completely satisfactory, fulfilling all the requirements for a very definite service. The danger lies in the probability of their being carelessly described thru publication and their ultimate use where conditions are wholly different.

More regrettable are the numerous mere indications which form the basis of comparison for those small consumers who lack the means of making more reliable tests. The great majority of small consumers purchase their cells by amperage readings, selecting that cell which is superior in this respect. That this practice is far from reliable will be brought out later. As stated previously, a purchaser must either test cells for himself or accept the guarantees of the manufacturer. To the small consumer, who secures a half dozen cells, or even a barrel of them now and then, the latter alternative is the only one open. The expenditure for apparatus and number of cells necessary for testing in a reliable manner are too large in proportion to the total number of cells procured to be justifiable. It would, therefore, be better policy for such a consumer to obtain cells which he knows to be the product of a reputable and reliable house rather than to rely upon the indication of his pocket ammeter.

Results of the Non-uniformity of Dry Cell Tests.

The diversity in the methods of testing cells is very troublesome for both the manufacturer and consumer. The former is often called upon to guarantee the service of his product when subjected to certain tests which have little or no relation to any which he may have adopted. We recall one such specification, which called for a guarantee of current output and working voltage at any stated time throughout a test which subjected 2 cells in series to a discharge thru 15 ohms resistance for 5 minutes each quarter hour for 7 consecutive hours, the cells being allowed to recuperate during the remaining 17 hours. This test was used by a consumer as the basis for purchasing cells for use in telephone service. It differs quite markedly from the test considered as standard by the large consumers of cells for telephone service in this country. It was undoubtedly designed to suit the convenience of the customer, being continued thruout the working hours of the day.

Although it is not impossible, it does become quite difficult for a manufacturer of dry cells to calculate from the results of his regular tests just what may be expected of his product when subjected to a particular test required in the specifications of his customer. The difficulty perhaps lies not in the method of the consumer, for, as in the example cited, that may be as representative of the service and as reliably carried out as any other telephone test. The difficulty lies in the fact that the two methods are not easily comparable. The adoption of some standard tests which would hold between manufacturer and consumer alike would be very advantageous to both. The establishment of such tests and the publicity which would thereby be given to the

Fig. 1 Short Circuit Current vs Service Capacity.

whole subject of testing would, we think, decrease the tendency of the small consumers (who, taken collectively, must use a considerable percentage of the output) to place reliance in the so-called tests which now form the basis for their judgment of a brand of cell, such as amperage or voltage readings. The lack of relationship between short-circuit current and service has been brought out clearly in previous papers given before this Society, and we give Fig. 1 in order to emphasize this point. The full line has been drawn thru points which represent the service capacities of eight brands of cells now upon the market, represented by letters A, B, C, D, etc. The broken line is drawn thru points representing the initial short-circuit currents of the same

cells. The values in all cases are expressed as percentages of the service capacity and short-circuit current of brand A, which is given the value of 100 for convenience. Each value represents the averages of 10 different tests of six cells each, completed at monthly intervals during 1910.

From this chart it is evident that there is in no sense a relationship between service and short-circuit current. It is true that the amperage reading of a cell, coupled with a familiarity with the particular brand, does serve as a good indication of the age of the cell or the presence of any serious defect; however, the customer who judges solely from the short-circuit current is very apt to obtain inferior quality, and yet we are informed by dealers that at least 90 percent of the customers who buy cells off the shelves demand that they be so read and in most cases select that brand giving the higher current.

We wish to call attention also to the type of the service tests which are recommended in various publications, tests which are not only unreliable, but which are absolutely misleading. We quote from one of the publications of a manufacturer of a brand of cell quite well known. "Short-circuit a cell for 15 minutes and watch how it recuperates after 1 minute, 15 minutes, 1 hour, 24 hours. The cell giving the best results after 24 hours is the best, especially for telephone work." Such a test might well be used as representative of some of the heavier services, but for telephone work it is meaningless.

In the correspondence column of one of the monthly gas engine journals, we have noted the following answer to this inquiry:

"What should dry cells test, and what is the best test?"

Answer:—"Dry cells should test from 1 to 1½ volts each when new, and from 15 to 30 amperes. The voltage and amperage tests are the only ones we know of for dry cells."

We have recently seen the statement, in a similar publication, that with a little practice one may become proficient in judging the cell by short-circuiting with a nail or other sharp-pointed instrument, the point being brought into contact with the carbon electrode. Dependent upon whether there resulted a "tiny spark, accompanied by a little puff of smoke," or simply a "black mark upon the carbon," the cell is to be judged as good or bad. This

process may serve to locate a cell which accidentally or otherwise has become valueless, but it will not separate the fresh good cell from the equally fresh poor one.

We cite such examples simply to emphasize the need for informing the consumer and for standardizing the methods of carrying on dry cell tests.

The Requirements for a Satisfactory Test.

Let us consider, then, the requirements of a satisfactory test for dry cells and the conditions which have the greater influence upon the results obtained.

In general (other than for purposes of research) there are but two reasons for desiring a test upon dry cells:

1. To ascertain what life may be obtained from a brand of cells in a certain service.

2. To ascertain which one of several brands will give the longest life in that particular service.

With the former object in view the knowledge is best obtained by actual use of the cells in connection with the appliance. In some cases this is the only feasible way in which the definite information sought can be obtained. The great majority of tests are carried on, however, with the second object in view, *viz.*, the comparison of two or more brands of cells for use in a particular service. Where the amount of testing is large, it is impossible, even were it expedient, to use the actual appliances for testing cells, and it becomes necessary to devise special testing methods and apparatus such that results obtained therefrom shall be comparable to the results obtained from the cells when placed in actual service. This is, we take it, the one necessary condition which dry cell tests must fulfil.

There have been tests devised which seek to go further and make the operating conditions not only comparable, but as similar as may be to the operating conditions of the service for which the test is intended. Upon this point there is some diversity of opinion. Some authorities claim that a test is of greater value and is more reliable the more nearly the conditions of test approach those of service, and, following out these claims, have devised certain tests which are rendered quite complicated, requiring much attention and apparatus for their continuance,

by the introduction into the method of some of the irregularities to be expected in service. It is questionable, however, if results of greater meaning are obtained from such strict adherence to service conditions. At best, such a test is but an approach to actual service, which must be continually varying from time to time and from locality to locality. Again, the apparatus necessary to carry on an irregular, intermittent test is very complicated and requires much careful attention. This feature limits its use to the large consumers and manufacturers.

We are often asked regarding the advisability of testing various brands of cells by connecting them in series and discharging them simultaneously.

There are several objections to this method. If the cells are discharged thru a constant resistance, as is generally the case, the results may become very misleading. Consider two cells, A and B, A being of superior quality, connected in this manner and discharged thru 10 ohms. Assume that at the beginning of the test the cells each give a working voltage of 1.4 volts, or 2.8 total working voltage. The drain on the cells would be 0.28 ampere, as would be the case were each cell connected separately thru 5 ohms resistance. The cells, being of unequal quality, will deteriorate at different rates. If we examine the conditions when, for example, cell A has reached 1.00 volt and cell B 0.75 volt, we find the similarity between the series and individual methods of testing has ceased. At this point the total working voltage of the series is 1.75 volts, producing a drain on each cell of 175 milli-amperes, while were the cells being discharged separately thru 5 ohms each, cell A would suffer a drain of 200 milli-amperes and cell B a drain of but 150 milli-amperes. When cells are tested in series thru constant resistance the poorer cell is drained more rapidly than would be the case were it connected separately thru half the resistance, while the better cell is drained to a less extent. In other words, the cells must be looked upon as being discharged separately thru resistances no longer equal, but proportional to the working voltages of the separate cells. Thus there is a constantly increasing advantage for the better cell and a like disadvantage for the poorer cell. From this method of testing, a qualitative classification of cells

may be made, but the results obtained will not show the quantitative relations of their service capacities.

This objection does not hold when the current drain is kept constant thruout the test. For practical purposes, however, we are not inclined to favor the constant current method in testing dry cells, for the great majority of appliances with which dry cells are used have either fixed resistances or are roughly adjustable, so that a test of this kind differs markedly from service conditions.

In general, we would advise against the testing of various brands of cells by connecting them in series. There are occasions, however, when this is the only method to employ. Especially is this true when test conditions, such as length of contact and recuperation periods, strength of current and temperature of the battery, cannot be held constant for the separate testing of various brands. It is much preferable, for instance, to use the series method of test upon an automobile than to test the various brands upon different machines or upon the same machine at different times.

The Effect of Temperature Upon Dry Cell Testing.

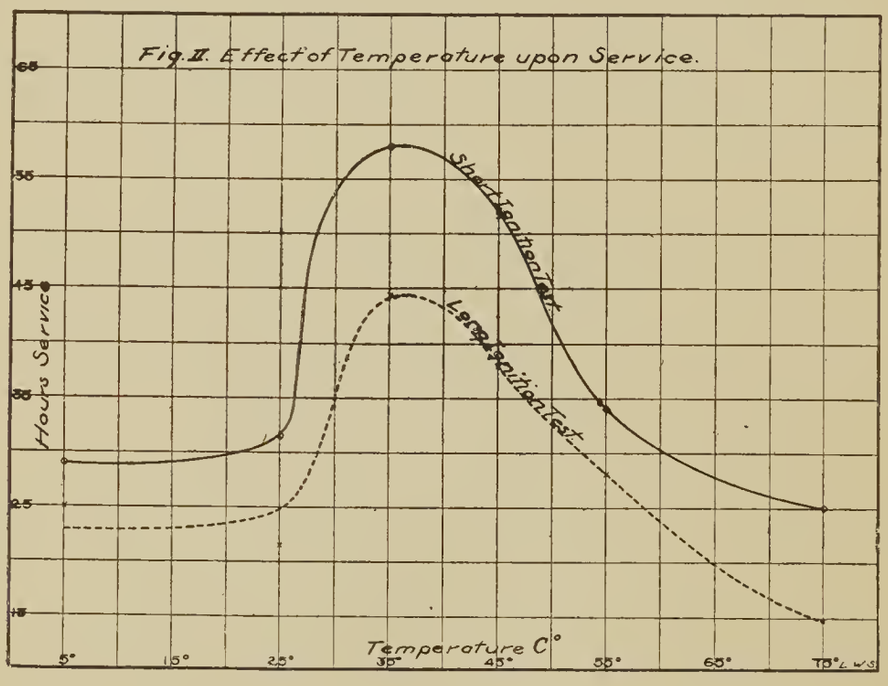
Temperature is a most important factor in dry cell testing, and a large part of the non-uniformity in the results of tests may, we think, be traced to temperature variations.

Effect on Short-Circuit Current.—We have heard customers complain that cells received were defective, giving such low amperage as to make them unsalable. An investigation often shows that the cells have been standing in a very cold place, and that when brought to normal temperature, the cells give very satisfactory currents. The following table shows the value of the average current of a lot of 10 cells read at different temperatures.

Temperature	Current	Amperage Difference
—10° C.	13.7	
0 "	16.4	2.7
10 "	18.4	2.0
20 "	19.8	1.5
30 "	20.9	1.1
40 "	21.8	0.9
50 "	22.4	0.6

It is seen that the differences in amperage increase rapidly as the temperature becomes lower, which explains very satisfactorily the above conditions. Hence, in reading the amperage of a cell, a correction should be made for temperature.

Effect on service.—The influence of temperature upon service is greater than is generally supposed. Where comparable results are desired, it is of extreme importance that the two batteries be kept at the same temperature. The effect is very markedly shown by the results obtained from a test representative of ignition service carried on at 7 different temperatures, *viz.*, 5°, 25°, 35°, 45°, 55°, 65° and 75° C. These tests were all made at the same time and with the same brand of cells, taken from the same lot of manufacture. These results are shown diagrammatically in Fig. 2, the two curves representing similar



tests, the length of closure differing somewhat. The great variations obtainable between 15° and 35°, between which values practically all testing is done, makes the importance of temperature regulation very evident.

The effect of temperature also varies with the nature of the service, high temperatures giving longer service where the drain is heavy, while low temperatures are favorable for light drain service lasting over a considerable period. This effect is shown in the following table, the figures representing hours of service

given by cells connected continuously thru various resistances as shown, at four different temperatures. The tests were continued until the working voltage fell to 0.5 volt. The maximum value for each resistance is underscored:

	Ohms Resistance					
	2	4	8	16	32	40
0°	40	80	270	560	1800	2550
25°	60	94	260	700	1550	1630
50°	70	160	350	650	1250	1420
75°	65	158	315	615	1390	1510

Effect of Storage.—Of prime importance in dry cell testing is a knowledge of the effect of temperature upon the rate of deterioration of cells when left on open circuit. To determine just what this effect might be, a number of cells were stored at seven different temperatures. The following table gives the initial currents and the drop in amperage after 10 weeks, expressed as a percentage of the initial values.

Temperature	Initial Amp.	Per cent. drop in Amp. in 10 weeks
5°C.	18.1	4.4
25 "	22.0	10.0
35 "	21.0	19.0
45 "	22.8	25.0
55 "	23.0	52.0
65 "	20.5	71.0
75 "	21.0	98.0

The greatly increased rate of deterioration on open circuit at high temperatures no doubt accounts for the poor service obtainable at such temperatures over long periods of time. A knowledge of this effect of temperature would undoubtedly explain the cases, which are at times brought to our attention, of cells rapidly deteriorating upon a dealer's shelves, from "no cause whatever."

The cells should be stored in a dry, cool place, and not in the corner behind the stove.

The Rating of Dry Cells.

In interpreting the results obtained from a test of various grades of cells, we wish to caution against drawing definite conclusions from the outcome of a single or a small number of tests. When the matter of choosing a brand is of much im-

portance, it is necessary to run a series of tests over a period of six months or a year. In this way a very good idea may be obtained of the average service results which may be expected.

In the following table are given the results of 10 monthly tests completed during 1910 on two brands of dry cells. The values represent the length of service given:

Tests	1	2	3	4	5	6	7	8	9	10	Average
Brand A.....	42	35	38	33	60	45	48	35	66	48	45.0
" B.....	30	37	24	25	27	40	48	42	40	40	35.3

It is very evident from a comparison of the averages of these tests that Brand A is much superior to Brand B, yet had the consumer only the results from tests 2 or 8, he would have undoubtedly arrived at a very erroneous conclusion regarding the real merits of the two brands.

In regard to the terms in which the results of dry cell tests should be reported, there is some difference of opinion, some authorities contending that the ratings should be expressed as the number of ampere hours given by a cell under specified conditions to a certain working voltage value. Others claim that more practical meaning is attached to a statement of the length of time during which the cell is able to maintain its working voltage above the specified limiting value.

It is our opinion that that method of rating should be used which gives to the consumer the exact information which he desires, hence we favor the rating of cells by the length of service of a given kind which they are capable of giving.

It is perfectly evident that the consumer is interested in the length of service which he is able to obtain from a battery, and not in the amount of energy given. At first thought it might appear that the ampere-hour capacity of a dry cell bears such a relation to length of service, that either method of rating would give the same information. Such is not the case, however. Differences in discharge rate cause vast differences in the number of ampere hours obtainable from the cell. From the nature of the discharge curve, it is quite difficult to calculate the length of service obtainable under the conditions limiting the ampere-hour rating, while to go further and deduce from the rated ampere-hour capacity under one set of conditions, the output

to be expected under different conditions becomes a hopeless task. Equally hopeless is the final interpreting of the result in terms of length of service.

Again, a dry cell does not always give length of service which is proportional to ampere-hour output. It is easily possible to produce two dry cells which will give equal lengths of service, the ampere-hour output of which will show marked differences. Hence a statement of the ampere-hour capacity of two brands of cells is very apt to be misleading, as it does not settle definitely which is the better cell to use upon a given service.

For research purposes the energy or ampere-hour output of a cell is very useful, but as a practical rating for dry cells it is not satisfactory, especially from the standpoint of the consumer.

Recommended Tests.

In the foregoing pages we have pointed out the cause for and results of the lack of uniformity in the methods of testing dry cells. We are of the belief that an adoption of tests which might be accepted as standard by consumer and producer alike would be of direct benefit to all concerned. Some time ago a committee was appointed by this Society for the purpose of ultimately bringing about such a standardization. We would like at this point to propose for consideration certain tests covering the two most important services, namely, telephone, and gas engine ignition.

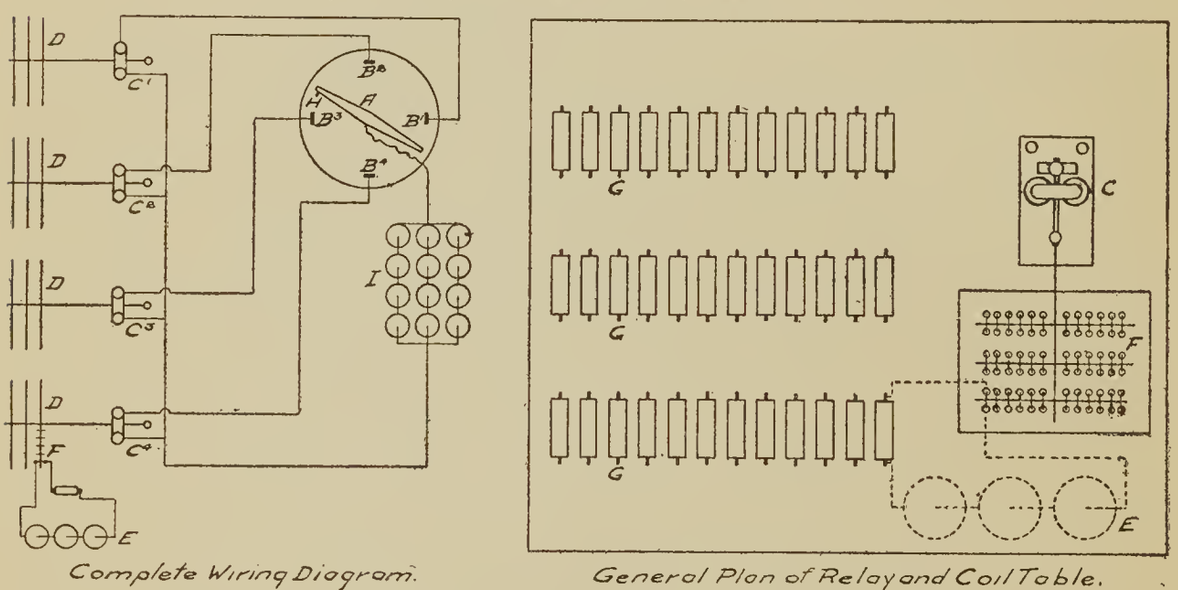
The nature of these services was fully outlined in papers delivered before the Society by Dr. J. W. Brown[1] and Mr. D. L. Ordway,[2] and therefore will be touched upon only in so far as is necessary to establish the relationship of the service to the tests which we propose.

Telephone Service.—The battery circuit of the telephone consists of the transmitter and the primary winding of an induction coil, the secondary of which sends the impulses to the line. The total resistance of the circuit varies from 15 to 20 ohms in different installations. It is customary to use two or three cells in series, the tendency being to favor the latter number, and it is recommended by one of the important telephone companies that the battery should at all times give a current of more than 0.14 ampere at the end of one minute after the battery has been

[1] Trans. Amer. Electrochem, Soc., 13, 173 (1908).
[2] Trans. Amer. Electrochem. Soc., 17, 341 (1910).

disconnected from the transmitter and connected in circuit with an ammeter and a resistance of 20 ohms. This specification necessitates that the working voltage be constantly 2.8 volts or more. It is probably true that satisfactory service may be obtained at a much lower working voltage, but thru conservatism this end point has been established, and the cells are as a rule removed by test. Although accuracy of method is of primary importance, simplicity and adaptability should not be overlooked in the selection of a suitable test for general adoption. We have been using for some time a test which requires a minimum of care and supervision and which is quite comparable to the more complicated tests. It subjects 3 cells in series to a discharge thru 20 ohms resistance for a period of two minutes each hour,

Fig. III. Telephone Test For Dry Cells.



Complete Wiring Diagram. General Plan of Relay and Coil Table.

during 24 hours per day and 7 days per week, until the working voltage reaches the limiting value of 2.8 volts, the results being reported as the number of hours' service to this cut-off point.

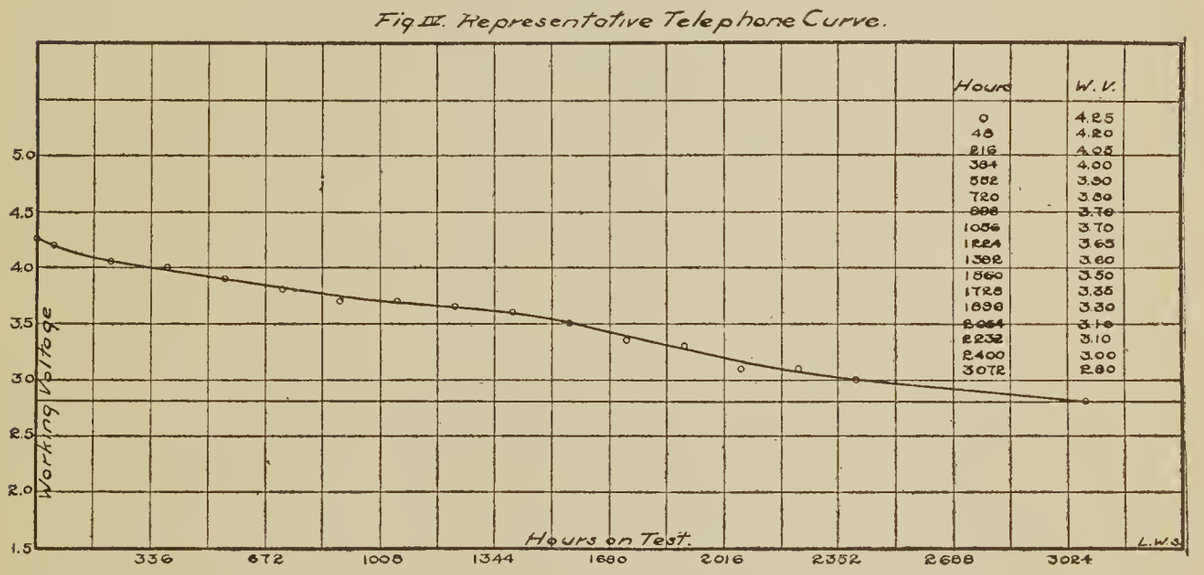
The energy drawn from the battery in this test is approximately equivalent to that consumed in the more complicated methods, the batteries give practically equivalent periods of service, and the number of cells, resistance in circuit, and cut-off point are identical.

The regularity of this test which we propose eliminates the mechanical appliances necessary to obtain decreased night and Sunday service. The left-hand portion of Fig. 3 shows diagrammatically the apparatus necessary and its arrangement. The

hand of the clock A revolves once per hour, closing by means of the contact H the circuit of battery I in turn thru the contacts B, B_2, B_3 and B_4. This current magnetizes the cores of the telegraph relays C, C_2, C_3 and C_4, causing the extended armature arms D to fall, bringing the inverted U-shaped fingers F into mercury cups, thru which the test battery circuits E are closed. Each contact B is of such length that two minutes are required for the passage of the contact H.

At the right of the figure is shown the arrangement of the relay and coil table. The test batteries are stored underneath the table and are read from the mercury cup F.

Fig. 4 shows a representative discharge curve obtained from a battery of three 2½ x 6-inch dry cells of a well-known brand.



The curve passes thru the values of the working voltage at the end of the discharge periods.

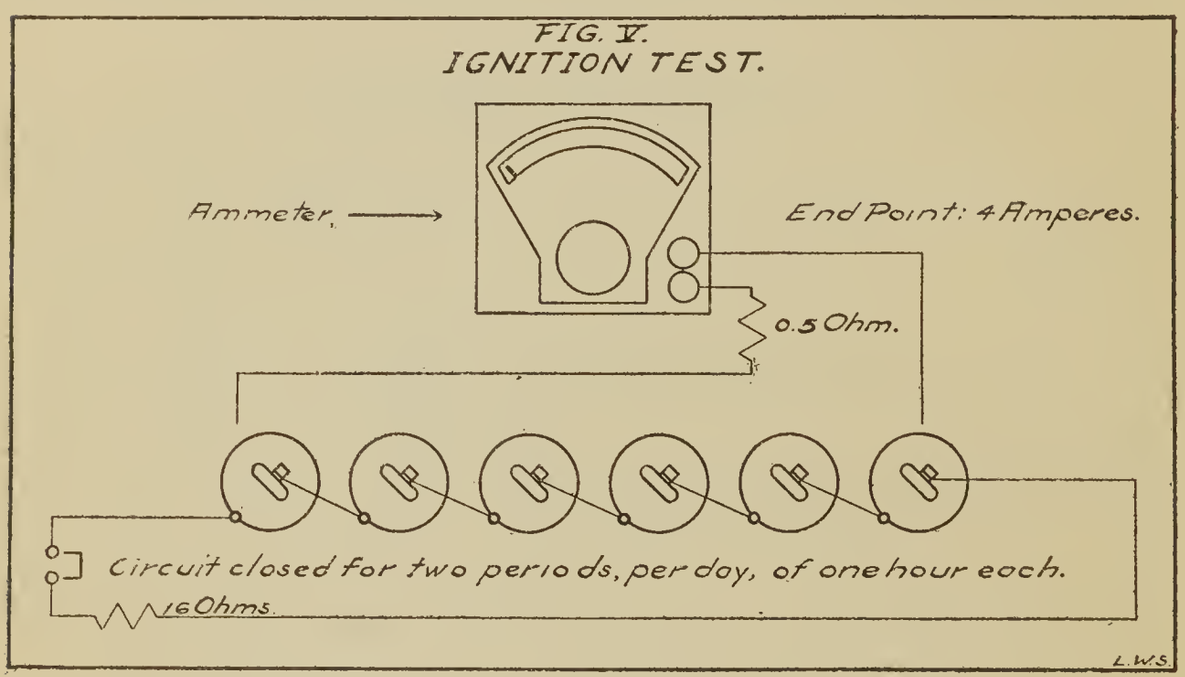
Ignition Service.—Ignition practice also presents great diversity in operating conditions, and formulating a satisfactory test to meet the demands requires much consideration of the various systems used.

It is impossible in the scope of this paper to enter into a discussion of the ignition question, one with which all are more or less familiar. We wish here only to outline briefly the results of our investigations in this field. In developing a test suitable for this service, we used a 4-cylinder automobile engine, equipped with a standard make of spark coil. With different numbers

of cells in series, resistance was cut into the circuit until the engine failed to operate satisfactorily. We thus reached the limits of satisfactory ignition for these particular conditions. Readings at this point were taken of the working voltage, average drain on the battery and the value of the impulse which the battery was capable of forcing thru the primary winding of the spark coil.[3]

The work was then duplicated, using in turn all the leading makes of coils. Thus we were able to formulate what may be considered as average limiting conditions of actual ignition service.

It was found that in the majority of cases 5 or 6 cells in series gave ample voltage. Efficient service was obtained in



some cases with as low a drain on the battery as 0.2 or 0.3 ampere. It is very probable, however, that 0.5 ampere more nearly represents the average drain which could be maintained by the adjustment of coils without proper instruments.[4] A battery was found to give inefficient service when the impulse of current which it was able to send thru the primary winding of the spark coil fell below 2 or 3 amperes.

From these findings we have developed the following test, which we have adopted as our standard for ignition service. A

[3] A full discussion of the impulse value and its importance in ignition service is contained in: D. L. Ordway, Trans. Amer. Electrochem. Soc., **17**, 361 (1910).

[4] The value of the approximate drain, viz., 0.5 ampere, does not apply to the various single spark appliances now to be obtained, which are much more economical of current.

battery of six cells is connected in series with a 16-ohm coil, which permits an average drain on the battery thruout its life of approximately 0.5 ampere. Readings of the working voltage are taken at intervals thruout the test, the most important reading, however, being the impulse of current which the battery is able to force thru a ½-ohm coil connected in series with the ammeter and in parallel with the 16-ohm resistance. When this value at the end of a period of contact falls below 4 amperes, the battery is considered unfit for service and discarded. This value is taken, rather than 3 amperes, in order to be conservative. We have thus duplicated all conditions adopted from our investigation as representing the average ignition service. In settling upon the length of time during which the battery should be discharged, we interviewed many users of automobiles, and the consensus of opinion was that, after the novelty of an automobile wore off, the length of time during which a car would be in operation would average not far from 2 hours a day. Our test batteries are therefore discharged for this length of time each day, divided, however, into two periods, one hour in the morning and one in the afternoon. As a test for lighter service, we sometimes subject the battery to two drain periods of ½ hour each. If the amount of testing be not too great, the circuits may be closed by hand, in which case no apparatus is needed other than instruments for reading, a number of 16-ohm resistance coils and a 0.5-ohm coil for use in taking the impulse readings.

We have used this test satisfactorily for several years, and believe it to be more trustworthy, easier in application and more representative of service conditions than any test which has come to our notice. By slight variations, chiefly in the time of discharge, it may be made representative of any system of various types of ignition service.

Shelf Life Testing.—Since it is often the case that quite an interval of time may elapse between the manufacture and installation of a cell in service, a knowledge of what may be expected during this period becomes of no little importance, and hence an open circuit or "shelf life" test is quite essential.

The ideal method for such a test would be the determination of the decrease of service capacity due to storage over definite

periods. This practice, however, would entail much labor and expense where the amount of testing to be done is large.

The method generally employed to determine shelf life consists of reading the initial voltage and short-circuit current of a representative sample of cells, followed by current readings at intervals of one or two months, depending upon the nature of the cells in question. The ammeter for reading short-circuit current should be dead beat, and with its leads should have a resistance of 0.01 ohm. Two 30-inch lengths of No. 12 lamp cord make very convenient leads. The results are merely indicative of increase in internal resistance, and bear no definite relation to the service which the cells may give. However, this information, coupled with familiarity with a brand of cells, becomes a very good indication of its quality. It also serves to indicate any serious defects of manufacture. The cells are kept on the shelf until the short-circuit current has fallen below 10 amperes. This point is arbitrarily chosen, as it represents a point below which it would be difficult to market the cell. For practical purposes, the results are expressed as the number of months during which the short-circuit current remains above this cut-off point. Much more meaning, however, is attached to the rate at which the current falls, generally reported as the drop in amperage expressed as a percentage of the initial amperage. This is especially true when investigation of the quality of cells is the object. For practical purposes, however, the first rating given, *i. e.*, months to 10 amperes, is perhaps preferable.

There are, of course, many miscellaneous services in which dry cells are used, tests for which must be formulated as occasion demands and to suit the particular needs of the case. For the more important uses, however, *viz.*, telephone and ignition services, we trust uniform methods of testing may soon be adopted which will be satisfactory to all.

Research Laboratory,
National Carbon Co.,
April, 1911.

A paper read at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 7, 1911, President Wm. H. Walker in the Chair.

THE TATE BIFUNCTIONAL ACCUMULATOR PLATE.

By Alfred O. Tate.

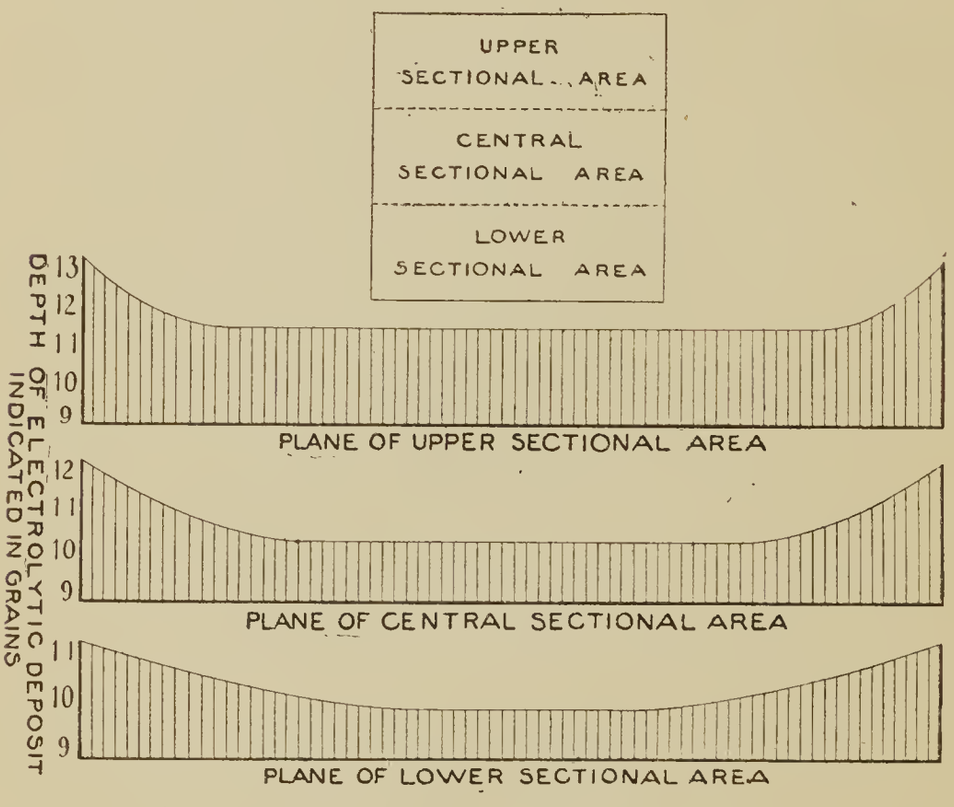
An exposition of the functions of this plate involves the art of storing electricity through the medium of the electrolytic cell. Its structural features show a radical departure from mechanical methods heretofore employed, and as these were evolved with the object of harmonizing the relations between certain electrochemical phenomena and the instruments utilized for their production in the practice of the art referred to, it has been suggested to the writer that an exposition of some special features of this plate would be equally as interesting to the electrochemist as to the electrical engineer.

The Tate Bifunctional Accumulator does not embody any new chemical principle. While the plate may be adapted to utilize any of the well-known combinations identified with the art, it has been deemed desirable to adhere in practice to the reactions between lead oxide and metallic lead, as produced through a dilute sulphuric acid medium.

The plate is termed "Bifunctional" because it contains within itself the positive and negative elements, and is therefore capable of performing two functions. The plates heretofore employed in the art are each capable of performing but one function—that either of the positive or negative element—and may therefore be designated as "Unifunctional." Apart from its envelope or supporting medium, the feature which differentiates the Tate Bifunctional plate from more conventional forms heretofore employed is the substitution of short, narrow conducting strips, or ribbons for plates, or grids of relatively large superficial area.

Some of the reasons underlying this substitution may be best explained by reference to an experiment in electroplating, conducted with the object of demonstrating the conditions most largely responsible for the production of unequal current densities

in unifunctional plates of relatively large area, from which arises the obstructive reaction commonly termed "sulphating" under normal service conditions. When two unifunctional plates provided only with upper terminals are in electrical contact through an electrolytic medium, the line of least resistance between them describes a path located above their horizontal centers and along their vertical and horizontal edge areas, where so-called extraneous stream lines are given off. That is to say, the flow is heavier above than below the horizontal centers in all corresponding parts of the plates. As the vertical central regions are



approached, the densities become relatively lighter through the whole plate length, suggesting that current flow, somewhat like magnetism, has a tendency to seek the more extreme or outermost sections of a conducting medium of plate form. These conditions appear to be demonstrated by the following experiment in electroplating.

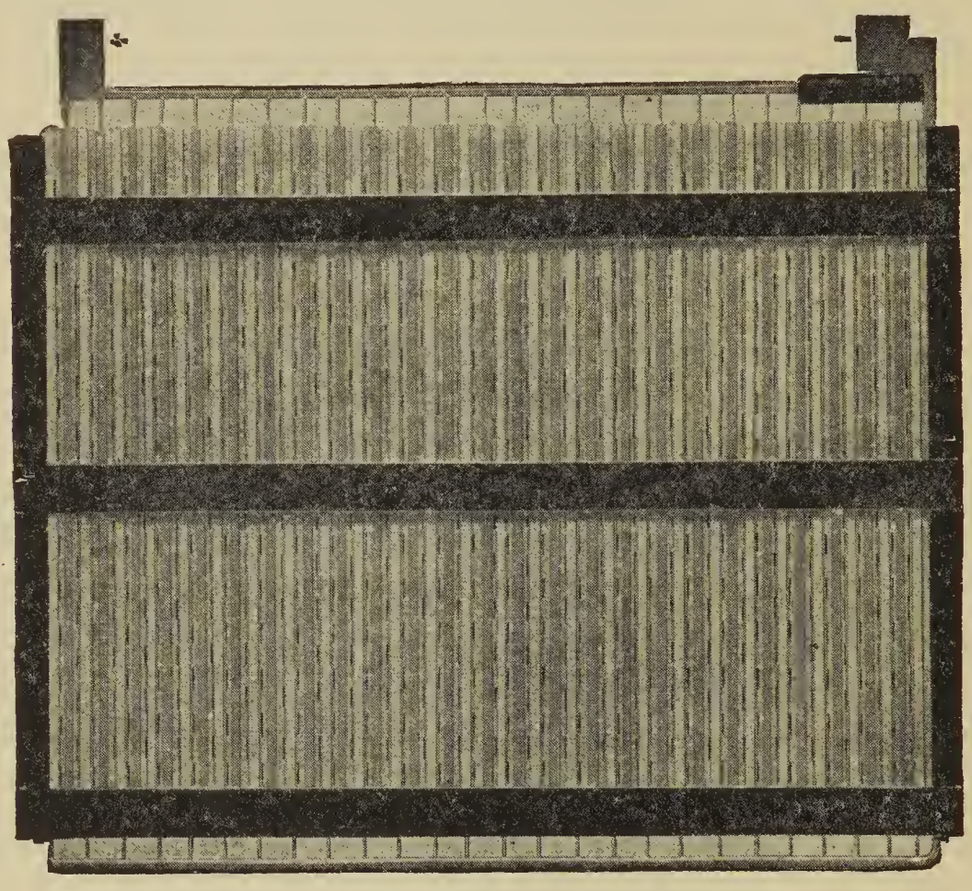
A thin copper plate, 18 inches square, was divided into 72 longitudinal sections of equal width. It was again divided into three planes of equal area by two indented horizontal lines drawn at points equidistant from top and bottom and from each other. It was then immersed in a cyanid of copper electroplating bath,

distant 3 inches from an anode plate of the same superficial area, both plates being in contact with the outer circuit throughout the whole length of their upper edges, and subjected for six hours to a current of 10 amperes at 4 volts. A strip of the original sheet, of exactly the same dimensions as one of the longitudinal sections of the plate, was divided into three equal parts, each of which was found to weigh 9 grains, thus indicating the weight of each subdivided longitudinal section of the complete plate before immersion. After immersion for the stated period, the plate was removed and dissected. Each longitudinal strip was cut into three equal parts, as indicated by the indented horizontal lines, and the weight of each part ascertained and recorded in consecutive order, so as to indicate the distribution of the electrolytically deposited material over the surface of the three equal plane areas into which the plate was originally subdivided. It was observed that the uppermost plane area had acquired the heaviest deposit, and that electrolytic action decreased constantly as the lower section of the plate was approached. Each of the three sections showed a marked rise in the weights of deposited material in the direction of their lateral edges.

Inasmuch as the quantity of matter precipitated, deposited or transmuted in an electrolytic cell bears a fixed relation to current quantity and time, and as time was equal with regard to the results of deposition exhibited in these three sectional areas, it follows that current density must have been unequal in different sections of the plate. When these conditions are viewed in their relation to the operation of storage battery cells of the unifunctional plate type, an explanation may be found for under-working or inactivity in certain sections of the grids and the consequent appearance of the obstructive phenomenon commonly termed "sulphating" under normal service conditions.

It is obvious from this visual demonstration that by decreasing the distance between the lateral edge areas of a conducting medium of plate form, in other words, by restricting its width, equalization of current density in a horizontal direction may be more closely approximated, for the reason that this narrowing process tends to eliminate or restrict the extent of those relatively remote central regions which are partially responsible for unequal current densities in conducting plates of relatively large superficial areas.

In the Tate Bifunctional plate the current finds entrance at the top and exit at the bottom of a finely-subdivided, multiple-assembled unit provided with an alternating series of anode and cathode conducting strips or ribbons, each 8 inches in length. There can be no appreciable variation of current density above or below their horizontal centers in a vertical direction, owing to the top and bottom method of connection, which equalizes potential between all corresponding working surface sections of the plate above and below those centers. The width of these conductors



STANDARD TATE BIFUNCTONAL ACCUMULATOR PLATE

with the applied active material is ⅜ of an inch, thereby effecting equalization of current density in a lateral direction, as previously noted. It will thus be seen that these extremely short and narrow conducting strips, assembled in close multiple relation and connected with the outer circuit alternately top and bottom, achieve the equalization of current density over all the active surfaces of the unit with as great a degree of precision as it is perhaps possible to attain in the exercise of practical mechanical art. Thus the probable major cause of so-called "sulphating" under normal service conditions in accumulators as heretofore

constructed has been eliminated in these Bifunctional plates, and it was to achieve this object, together with others that will not be dwelt on herein, that short, narrow ribbon or strip conductors were substituted for the plate or grid formations that hitherto have been most largely employed in the practice of the art.

One other probable reason for the appearance of this phenomenon termed "sulphating" may be noted. In unifunctional plates of the Faure or applied oxid type, the active material has been frequently applied to the plates or grids in relatively thick masses. Later investigation appears to demonstrate that these masses are inactive beyond a certain limitation of depth under normal service conditions.

In "The Standard Handbook for Electrical Engineers, 1908," Lyndon, discussing storage batteries, states:

"The electrolytic action seldom penetrates to a depth greater than one-sixteenth of an inch (1.5 mm.) at ordinary discharge rates, so that where the thickness of the active material measured from the surface of the electrolyte to the conducting plate exceeds this amount, the portion in excess of this thickness is practically useless."

Two results of this condition seem obvious: First, that inactive material constitutes a dead resistance to current flow, thus curtailing the useful energy of the cell, and, second, that it represents a probable source from which may proceed the obstructive reaction under discussion. In the Tate plate the active material is applied in the form of films somewhat less than one-thirty-second of an inch (0.75 mm.) in depth.

The surfaces of the metallic conducting ribbons which receive the active material are knurled so as to present a multitudinous series of minute points and equally minute depressions. Through these means a high degree of oxidation over the knurled surfaces is effected under the process of forming, thus securing relatively perfect amalgamation and equally perfect and permanent contact between the conducting media and the superimposed active elements. The extreme shallowness of the active columns ensures their activity under all conditions of normal operation, and this, coupled with the amalgamated contact method, eliminates another probable cause of the phenomenon termed "sulphating."

In conclusion, a few words more with relation to relative depths of active material may be ventured as of interest to the electrochemist. They are, that the depth of the active mass appears to bear a significant relation to the time periods required to effect transmutation. This process seems to be achieved progressively from the metallic and electrolytic contact surfaces, in either direction, and to depend for consummation upon current density in conjunction with time. When the active elements are relatively deep, comparatively lower current densities and longer time periods are necessary. As these elements approach the condition of films, as distinguished from masses, current densities may be raised and time periods shortened.

This assumption appears to be amply sustained through the action of a Tate Bifunctional plate, which was discharged to zero and then fully charged in a period of thirty-five minutes, without resultant physical injury or impairment of subsequent normal capacity. These plates, with a capacity of 40 ampere hours on an eight-hour discharge rate, have frequently delivered 250 amperes on short circuit tests with similar results, and these conditions appear, therefore, to justify the above conclusions.

DISCUSSION.

DR. J. W. BROWN: What is the capacity of this new cell as compared with the older type, per unit of weight?

MR. A. O. TATE: The standard unit weighs about 4.5 pounds, with a capacity of about 75-watt hours. That would give about 16½ watt hours per pound. That is the bald element, stripped for an elemental test. In service batteries, the weight varies with the conditions of service, but it is usually about one pound per 11 or 12 watt hours.

MR. A. O. TATE *(Communicated)*: The capacity of the standard Tate plate is being steadily increased as the result of refinement of manufacture and the correction of detail due to the suggestions of practice. I can confidently state that this capacity will in the near future be worked up to at least 50 ampere-hours on an eight-hour rate, which will fix the efficiency of a service battery at about 15 watt-hours per pound of total weight.

A paper presented at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 7, 1911, President Wm. H. Walker in the Chair.

SOME UNSOLVED PROBLEMS IN ELECTROPLATING.

By George B. Hogaboom.

(Secretary of the National Electroplaters' Association.)

There has existed for such a long time a separation of the practical plater and the electrochemist that it is a pleasure to present this paper, as suggested by your secretary, and it is hoped that the practical end of electroplating, as represented by the National Electroplaters' Association, and the scientific end as represented by this Society, will be brought into a closer relation. As is well known, electroplating was the beginning of the science of electrochemistry, but it has lingered by the wayside and been neglected as a science, and today the unsolved problems are many.

Electroplating has been looked upon more as a trade than a science, and it is only during recent years that much study has been given to it by scientists, and that attention has been directed more to the electrolytic refining of metals than to the deposition of metal for decorative purposes. The solutions published by Roseleur in 1854 have been improved upon but little, and those who have published treatises upon the subject often give only a repetition of his formulas. Nickelplating, as invented by Dr. I. Adams, is probably the only exception.

The field is broad, but its development has been left to the practical man, guided only by "rule of the thumb." An electrochemist in the plating room of a factory is so rare that it probably can be said without fear of contradiction that they can be counted on the fingers of one's hands. The need today is mutual assistance in solving these problems and developing of new ideas. To a great extent they are "useless each without the other"—the plater producing results which he cannot duplicate—the electrochemist creating solutions that are not a commercial success.

So many phenomena have been encountered that to include the perplexing problems would necessitate a history of nearly every known solution and finish. The varying of the temperature and the electric current often prove a stumbling-block, and these conditions cannot always be controlled. There is a vast difference between producing a homogeneous deposit at a minimum cost from a solution where the amount of cathode surface is being changed every twenty minutes, and a solution in which the amount of cathode surface is always the same and the rapid deposit of the metal is more desired than a deposit that can be easily burnished. Such would be the difference, for instance, between the surface of a sheet of electrolytic copper and that of a cast lead and antimony electrolier with its deep reliefs and where a coarse crystalline structure would destroy its beauty. In the discussion of electroplating problems, it must be borne in mind that a mere deposit of a metal is not all, but that the deposit must be soft and smooth and lend itself to a decorative process; the anodes should be capable of being reduced easily; the electrolyte must offer little resistance to the electric current, and, last, but not least to the plater, who hears it so often that it becomes a part of him, the cost must be nominal.

The automobile industry has brought about, more than anything else, the need of a heavy deposit of brass. At present this is done in solution of cyanide of Cu and Zn. The deposit is not only slow, but unsatisfactory, because of what is known as "spotting out"—a discoloration in spots which appears on the work after it has been polished and lacquered. Deposits on cast metal give the most trouble. It is probably caused by the acids or alkaline solutions being absorbed in the pores of the metal, or in the small blow-holes, and the deposit covering these holes partially, leaving minute holes through which the solution oozes out. Several remedies have been suggested and tried, such as boiling out in some neutralizing chemical solution, placing in a drying oven for several days, but a satisfactory remedy has not been found.

An acid brass solution would be a great advantage. There is an acid copper and an acid zinc solution, but no acid brass electrolyte. The difference between the deposit from a cyanide

and a sulphate of copper solution well illustrates the advantage of having an acid brass solution.

Tin.—The formula for a tin solution published by Roseleur is the most generally used today, as little, if any, improvement has been made upon it, although a good solution which would give a heavy deposit is much desired. In Roseleur's solution the electrolyte is not replenished by the anode, but by the constant addition of a concentrated solution. This should be overcome, and would be appreciated by manufacturers of tinware.

Aluminum.—While several solutions have appeared from time to time for plating upon this metal, none of them are in general use, and a good electrolyte that would deposit gold, silver, brass or copper so that it would stand burnishing and not peel off in time could be used.

Nickel.—The successful removal of a deposit of nickel from another metal without affecting the latter has not been accomplished.

To give all the unsolved problems in detail would make a lengthy paper, and a simple statement of those most desired will be given:

An electrolyte that will remove the fire-scale from brass; also one that will produce a bright or a matte surface in place of using the present acid dips.

An electric cleaner that will saponify the grease and take it into solution instead of driving it to the top, where it has to be constantly removed to prevent it adhering again to the work as the latter is removed from the solution.

A heavy deposit of lead on the inside of iron pipes, to prevent rapid corrosion.

A method to coat electrogalvanized iron or steel with decorative metals without destroying the rust-resisting properties of the zinc.

An alkaline nickel-silver solution that can be worked with a low voltage.

A method of etching steel without destroying a resistance film of gelatine.

Some alkaline substance that would replace cyanide of potassium. This would be universally welcomed.

For the above suggestions, the writer is indebted to 100 dif-

ferent platers, who were kind enough to answer a request for unsolved problems. It may be interesting to note that 80 percent of them requested an acid brass solution.

DISCUSSION.

MR. F. A. LIDBURY: I consider this one of the most instructive papers read at the meeting, not only on account of the interesting list of problems presented, but because the fact that the list is so large suggests an interesting conclusion. I am inclined to believe that at least half the problems mentioned in this paper are comparatively easy of solution, and in connection with that it is a significant fact that practically all the advances in electroplating work that have come to the knowledge of this Society since its formation have been advances made by electrochemists working entirely outside the electroplating business; I need not refer to the work of such investigators as Prof. Bancroft and our President Walker. Now, is it not a fact that it is entirely the fault of the electroplating industry itself that this list of unsolved problems is so large today? Don't you think that, if electroplating works employed competent electrochemists to work continuously on these problems, more than half of them would be solved in the course of a year or two?

PRESIDENT W. H. WALKER: I believe that while they look to be unsolvable, it merely requires constant work on the part of a man fundamentally educated in the principles underlying these problems to bring about their solution.

MR. GEO. A. HOGABOOM: I would say that President Walker is absolutely correct in his statement. These problems are so important a factor in the electroplating business that a competent electrochemist should be engaged to investigate these troubles and to overcome them. When an electroplater goes into a place, if he cannot produce results, his employer will not go to an electrochemist and ask him to work the problem out—they will get a new plater.

PRESIDENT WALKER: All of which goes to show why the electroplaters have so many unsolved problems.

PROF. J. W. RICHARDS: I wish to say a word in commendation of the work which Mr. Hogaboom is doing as Secretary of the National Electroplaters' Association, and also of his colleague, the President of that Association, both of whom are members of our Society. They have gotten together the practical electroplaters to discuss electroplating in a practical way, meeting once a month here in New York City or its vicinity, and much good has been accomplished by their meetings. It is their endeavor to introduce scientific work into the electroplating establishments, and I know they will have our sympathy and co-operation; and this Society is going to get a great deal of help from them. Such reciprocal relation between the two organizations is bound to be of advantage to both.

MR. HOGABOOM: Supplementing Dr. Richards' remarks, it calls to mind what was said to me this morning by a gentleman, that it would be a grand thing if the National Electroplaters' Association could work as an auxiliary of the American Electrochemical Society. We are standing practically alone. We have to overcome a great many prejudices. Nobody but the electroplater realizes what an opposition there is against revealing any formulas. If you were in my position, and received the letters I receive protesting against the publication of formulas, you would not be surprised at the condition the electroplating industry is in today. If we could get the support of the American Electrochemical Society to assist in advancing the objects of the National Electroplaters' Association, I am very sure we would feel greatly pleased to do what we could to reciprocate. Dr. Richards has offered us help, and I am sure if we could have the help of all your members that the unsolved problems of electroplating would fade away. I know they can be solved, but the question is to interest someone sufficiently in them to have them solved.

MR. M. M. KOHN: I want to ask Mr. Hogaboom if he has had any experience whatever with plating platinum.

MR. HOGABOOM: Yes; that at the present time is one of the problems in electroplating. We have taken the old solution containing pyro-phosphate of sodium and tried to plate with it, but it has not been successful for a heavy deposit; for very light deposits it is successful. There are many jewelers throughout

New York City who are working with that solution. They take 10-karat gold jewelry and electroplate platinum upon it, and put is out as platinum-electroplated gold jewelry. I believe some platers are continually experimenting upon platinum deposits; but no one seems to be successful in depositing a very heavy plating.

PRESIDENT WALKER: In closing the discussion, I would like to anticipate a little and touch on the subject of my address tonight. I had occasion to write an article on "The Spirit of Alchemy in Modern Industry," and I wish I had had the splendid example which Mr. Hogaboom has brought out. The old alchemists made little progress—they worked for years and ended almost where they started. The primary reason for this lack of progress was the jealous secrecy engendered by selfish competition. As long as one keeps things absolutely secret within one's self, progress is impossible. Mr. Hogaboom brought out the fact that electroplaters guard very jealously their particular solutions, and that objection is made to the publication of any formulas. The moment we can get our industries to take a broader view, to be more altruistic and come out in the open, the sooner we can get the workers in the various industries to talk to their fellows and give them 1 percent of experience and get 99 percent in return, the quicker will real progress become possible.

A paper presented at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 7, 1911, President Wm. H. Walker in the Chair.

THE ELECTROLYTIC CORROSION OF ELECTROPLATED OBJECTS

By Walter S. Landis.

For several years past the author has been using a certain well-known brand of steel writing pen with great satisfaction. The demand made upon the pens is not severe, they being used only for signatures, corrections and such occasional writing, though being moist with ink for several hours at a time. Under such light and easy service the life of the pens was always at least a week, and frequently several weeks elapsed before they reached that scratchy stage demanding replacement.

This past winter, on attempting to purchase a fresh supply of this old, reliable brand, it was found that the local stationer did not have the plain steel ones in stock, but could furnish the same style and brand gold-plated. The cost of this plated pen was about one-half more than the plain steel ones. Thinking that the manufacturer had improved the life of the pen by this plating, a box of the new style was purchased. In use under practically the same service that the plain steel ones had been subjected to, the plated variety lasted rarely more than two days. The corrosion of the points and between the nibs was excessive, one pen frequently not writing more than five hundred words before requiring replacement. The life of the pens being so very short, I determined to make an investigation of the cause. The results of this investigation are here produced.

Microscopic and chemical tests showed that the pens were probably first copper-plated and then flashed with gold. The total thickness of the yellow metal coating was 0.006 mm., and the pens carried approximately 0.25 milligram of gold each. The plating was excellently done and was absolutely continuous as far as could be ascertained by chemical test. The pens could be thrown into sulphuric acid and left there for some time without

loss of weight. I therefore came to the conclusion that the corrosion was electrolytic in its nature, and formulated the following hypothesis to account for it: The friction of the pen point on paper rapidly wears off the plating on the point, thus exposing the steel. An electrolytic couple, *Steel—Ink—Gold,* is set up and corrosion of the steel takes place with great rapidity.

Some idea of the electrochemical nature of this couple may be gained from the following: A pen was stripped of its plating by an 18-hour immersion in strong potassium cyanide solution.

FIG. 1. Points of new gold-plated pen.

This stripped pen and a plated pen were then connected in series with a high resistance voltmeter and the two pens dipped into various kinds of ink, contained in a small cell about the size of a thimble. A potentiometer was not available at the time the experiments were made, so that I had to content myself with measurements made on closed circuits of 300 to 500 ohms' resistance.

When the two pens were dipped into "Barnes' National Jet Black Ink," the voltmeter showed a reading of 0.045 volt at

once, dropping in three minutes to 0.020 volt, and in five minutes to 0.015 volt, at which point it remained constant for some time. When taken out and redipped, the whole series repeated itself. Vibration of the pens, while immersed, gave a continuous reading of about 0.045 volt. The resistivity of the ink was approximately 112 ohms per cm. cube. Index of corrosion, 0.00040.

In "Stafford's Universal Writing Fluid," the series was 0.08, 0.02 and 0.008 volt; vibrating the pens maintained a constant

FIG. 2. Points of corroded gold-plated pen.

electromotive force of 0.022 volt. The resistivity of this ink was 68 ohms per cm. cube. Index of corrosion, 0.00033. In a rather old and faded brand of this ink, the reading under vibration of the pens was 0.016 volt. No measure of the resistivity of this faded ink was made.

In "Waterman's Ideal Ink," the series was 0.088 and 0.040 volt. A steady electromotive force of 0.120 volt could be maintained by vibrating the pens in the ink. The resistivity of this ink was 68 ohms per cm. cube. With a freshly stripped pen

against a fresh gold-plated one, a similar result of 0.12 volt was measured. Index of corrosion, 0.00176.

These experiments seem to corroborate my original hypothesis as to the cause of the excessive corrosion of the pens. When in use, the continued dipping of them into ink and the vibration occasioned as they rub over the paper maintains a short-circuited couple with the maximum electromotive force noted, and causes consequent corrosion of the steel point as the anode of this couple.

The "index of corrosion" as given above for the various writing fluids is the product of the maximum electromotive force found for the vibrated pens multiplied by the conductivity of the various inks. This index assists in choosing the least corrosive ink in case the plated pens have to be used.

While the corrosion of the plated pens is not a matter of great commercial importance, yet there is to be gained from the experience a certain wholesome lesson on the application of electroplating to the protection of less noble metals: *Do not plate with a nobler metal a material that is likely to be subjected to wear on one spot and which spot is to be moistened with liquids.* For, as soon as the plating is worn through on that spot, accelerated corrosion will take place, and in the end the resulting corrosion will be far worse than without the plating.

Electrometallurgical Laboratory,
Lehigh University,
March 1, 1911.

DISCUSSION.

PROF. J. W. RICHARDS: Prof. Landis was attracted by the fact that in buying some steel pens which had gold plate on them, they did not last as long as steel pens without the gold plate. He came to the conclusion that it must be electrochemical corrosion which was the cause of this. He examined the points of the pens and then the ink, and then determined the conductivity of the different kinds of ink. He suspended the pens in the ink, found the voltage on a closed circuit of high resistance, and found that

there was electromotive force between gold and steel in the different inks.

I call attention to his conclusion, which I think is a very useful one, that objects should not be electroplated if they are likely to wear through at one point, and there expose the base metal, which is more corrodable than the plate; because if the object is wet there, you inevitably have the electrolytic action.

Since the paper was published one of our members, Mr.

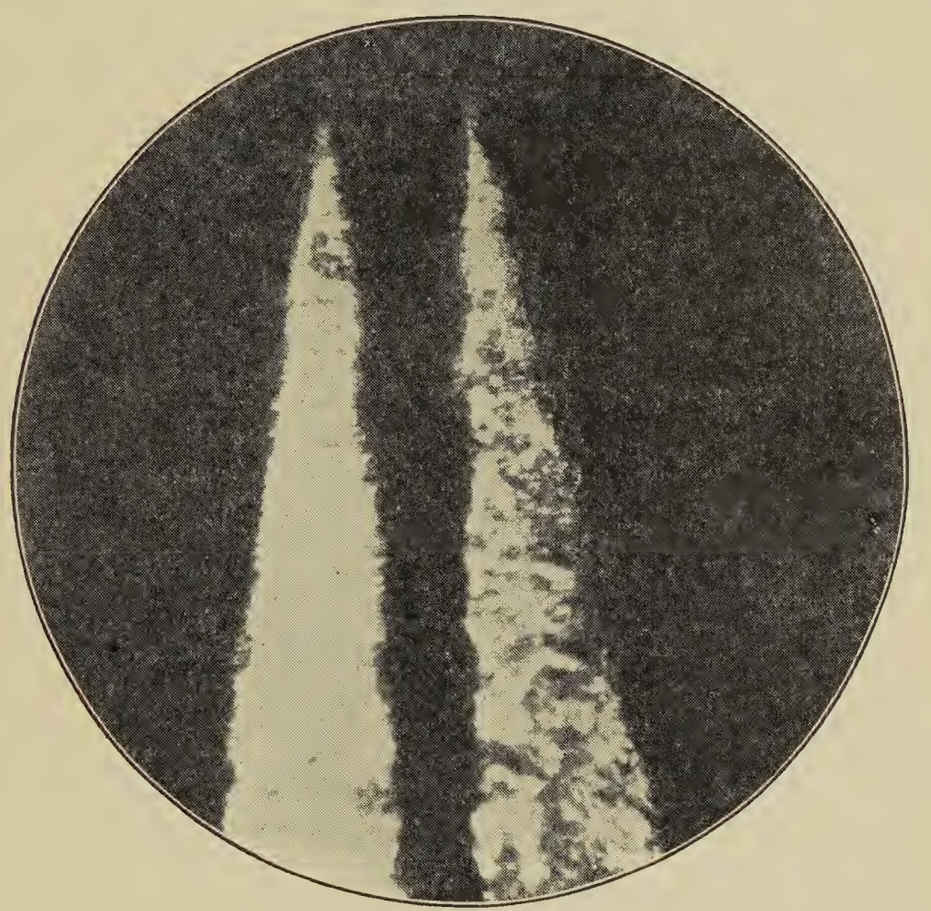


FIG. 3. Points of unused zinc-plated pen.

Murphy, said that he would zinc-plate some pens in order to protect the steel by the zinc. He zinc-plated some pens and sent them to us. If the pen is normally like Fig. 1, the point of the pen, after it has been zinc plated, is like Fig. 3. The slit in the pen is seen to be wider; it appears that the electrolyte penetrates there and the deposited metal opens up the slit in the pen, thus forcing the points of the pen apart and the pen becomes scratchy. The zinc-plated pens were scratchy and useless for writing; so that while zinc might theoretically protect the iron, it is imprac-

ticable to zinc-plate pens that way. Perhaps they might be zinc-plated by dipping in some manner, but not by electro-deposition.

PRESIDENT WM. H. WALKER: The dictum of Mr. Landis at the end of his paper sums up the experience of every one who has tried to protect iron or steel from corrosion by anything other than zinc or aluminum. In the lead lining of steel pipes, in ordinary tinplate, and in all the different methods which have been suggested for the protection of iron and steel by means of a magnetic oxide film, the conditions described by Mr. Landis are present.

DR. J. W. BROWN: I would like to ask Prof. Richards if the corrosion appeared anywhere else but on the points of the pens? Was the gold plate porous or non-porous?

PROF. RICHARDS: The corrosion apparently was confined to the points, and in the slit near the points of the pen. The pens were rather badly eaten away at those points. The rest of the coating did not seem to be acted upon. Evidently, when you commence to write with a pen the paper wears away the plating at the point, and the corrosion starts there, because the steel is exposed at the point, and it apparently travels through the points up into the slit, where, perhaps, the plating is not so perfect.

MR. CARL HERING: Will Prof. Landis please tell us what other explanation has ever been given for this corrosion? It seems to me that what he calls a new and "original" hypothesis is the one which has always been accepted for many years. I have never heard of any other. I have analyzed his corrosion factor and find it is nothing more than a measure of the current which flows, in terms of arbitrary units.

PROF. RICHARDS: I ask Mr. Hering if he has seen in print anywhere, or heard any one make, any statement as to the cause of the deterioration of these gold pens, before the matter was presented in this paper?

MR. HERING: Not as to pens, but I have heard the theory advanced in connection with other electro-plated objects. The words "galvanized iron" show that those who originally coated iron with zinc knew that the non-corrosion was due to an electric process, and that with the other metals for covering iron the electric current was in the wrong direction, hence favoring corrosion.

PROF. RICHARDS: When we are asked to pay fifty cents a gross more for gold pens than for steel pens, simply because they are gold-plated, it seems to me that this point is important, because apparently the life of the gold-plated pens is not as long as that of the plain steel pens.

MR. GEO. A. HOGABOOM: This subject appeals to me very much. We have noticed, as platers, if a piece of britannia metal is left exposed to the air without any metallic deposit upon it, it will not decompose, but if it is silver-plated the britannia metal will be decomposed very rapidly where the silver plate becomes worn off; and the peculiar thing about it is, that when you go to re-plate the article, it requires about three times the amount of voltage to get a deposit upon it as it did when the britannia metal was new.

If you take curved steel washers that have been passed through nitrate of potassium or oil for bluing, and remove that bluing by acid dips, and then electroplate them, you can break them with you fingers as fast as you want to. I know one man who plated 5,000 of these washers and when you put a slight pressure upon them they would break, while before they were nickel-plated they would stand quite a good deal of pressure. This probably is due to the same phenomena as in the case of the pen, it may be due to some form of electrochemical action.

PROF. RICHARDS: Don't you think the brittleness of the washers is due to the hydrogen which the steel absorbs from the chemical action during pickling?

MR. HOGABOOM: The peculiar thing about this is that if you take these washers and tumble them in emery and oil first, and then in leather, and plate them without passing them through any pickle of sulphuric or hydrochloric acid, the brittleness does not develop, but the minute you pass them through a pickle of any kind, the metal becomes brittle. The same is true of springs. This brittleness of the metal occurs more often if it is plated in an acid solution than if plated in a cyanide bath.

MR. F. W. WILLARD (*Communicated*): Mr. Landis has touched upon a problem vital to the manufacturer and user of metal plated hardware, especially nickel-plated iron and steel. Although the potential difference between iron and nickel is

less than 0.020 volt and the art of electroplating nickel has reached a high state of perfection, nickel plated iron or steel surfaces will invariably rust when exposed to moist atmosphere. High-grade nickel plating on Bessemer steel will rust in one week's exposure to atmospheres which prevail in the vicinity of New York City in the months of November, December, April and May.

Generally speaking, it might be claimed that the protective value of nickel for iron is a function of the weight of nickel per unit area of plated surface. In practice a second variable enters into consideration, namely, the continuity of the deposited coating. Practically, that continuity is beyond accurate control. From some 500 samples of nickel-plated Bessemer-steel punchings, I have been unable to find one piece which did not show distinct porous spots after five minutes exposure to ferroxyl reagent. The nickel on these punchings varied from 0.4 to 20.0 milligrams per square centimeter. No relation between the continuity, as indicated by the ferroxyl test, and the weight of nickel per unit area could be defined with sufficient precision to warrant publication of the data. One of the ideals of the user of plated hardware would be realized if he could insure the protection of his metal from corrosion by a specification covering the weight of protecting metal per unit area. Can it be done?

Dr. F. A. Wolff (*Communicated*): This paper was called to the attention of Dr. C. E. Waters, of the Bureau of Standards, who has had to deal a number of times with the amount of corrosion produced by different inks. For each test a carefully cleaned and weighed pair of pens was immersed in 25 c.c. of each kind of ink for 48 hours. In comparing a number of inks, all the pens were taken from the same box.

With red inks the corrosion was slight, amounting to 3 to 4 mg. for eosin inks and 15 to 30 mg. for erocein inks. Distilled water caused, in one experiment, a loss of 2 mg. The tendency with these inks was to corrode the pens in small spots all over the surface.

With black inks of the gallo-tannate of iron type, the pens lost from 22 to about 75 mg. for record inks, and as high as 275 mg. for one copying ink tested. The interesting point, however, was that even when two inks dissolved practically the same amount of iron, they did not always corrode the pens

in the same way. With one ink the entire surface of each of the pens would be uniformly corroded. With another ink, however, the attack was almost entirely along the edges, which became much serrated. In some cases the slits were so badly attacked that they were as much as one-half millimeter wide. These differences were not due to the individual pens, for in every case both pens of a pair immersed in the same ink were attacked in the same way. The pens employed were of a well-known standard make. They were of steel, with a bright finish, unplated.

PROF. W. S. LANDIS (*Communicated*): From the general nature of the discussion and the many letters I have received regarding my paper, I think most readers have simply taken it as a description of a rather novel experience as far as corrosion of pens is concerned. I was therefore rather surprised at the nature of Mr. Hering's remarks. I made no mention of originality in my application of the theory of electrolytic corrosion; when I spoke of "my original hypothesis," I simply meant my *first* hypothesis, *i. e.*, the first explanation that had occurred to me. I am also certain the electrolytic theory is not the only one so far proposed to explain such cases of corrosion. While I am an adherent of the electrolytic theory, I am not so unfair as to ignore the various others that have been proposed for the various types of corrosion met with in everyday life. Mr. Hering is certainly in error as to the origin of the word "galvanized," as applied to zinc-coated iron. Any encyclopedia or metallurgical treatise describes how the term "galvanized iron" arose from the original method of applying the zinc coating by the use of *galvanic* battery current, and that the name "galvanized iron" continued in use for zinc-coated iron even when the coating was applied by dipping the iron into melted zinc.

A paper read by C. T. Schluederberg, at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 7, 1911, President Wm. H. Walker in the Chair.

MERCUROUS PERCHLORATE ELECTROLYTIC METER.

By Frank C. Mathers and Albert F. O. Germann.

Preliminary Experiments.

Silver and copper are the metals which are generally deposited in coulometers (formerly called voltameters) for measuring the quantity of electricity which passes. A lead coulometer has been described.[1] Mercury, which has been employed by a few experimenters, possesses two great advantages over all other possible metals:

1. Mercury is liquid, so that the quantity which is deposited may be determined very rapidly by measuring it in a graduated tube.

2. Mercury has a very high chemical equivalent, so that a given current will precipitate a greater weight of mercury from mercurous solutions than of any other metal. The chemical equivalents of mercury(ous), silver, lead and copper (ic) are 200, 107.93, 103.45 and 31.8, respectively.

In spite of these apparent advantages, the mercury coulometer is not used in the laboratories, and the mercury electrolytic meter has only recently received serious consideration in commercial work. Perhaps the real reason for this limited employment of mercury coulometers and meters is the scarcity of suitable salts for making the electrolytes. Chlorides or sulphates of mercury cannot be used, because the corresponding mercurous salts are insoluble. Mercury does not form soluble compounds with the alkaline hydroxides. Salts with organic acids are not suitable on account of low conductivity of their solutions and instability during electrolysis. Mercurous nitrate has been tried,[2] but

[1] Betts and Kern, Trans. Amer. Electrochem. Soc., 6, 67 (1904).
[2] Hatfield, London Electrician, 60, 279 and 319 (1907-08).

decomposition of the acid radical caused its abandonment. A solution of the double salt, potassium mercuric iodide, is being tried at present on a commercial scale. The "Stia" meter[3] manufactured by Schott and Gen., Jena, uses this electrolyte. This meter is highly recommended by many people who have tested it for the company. The mercury is deposited upon an iridium foil, from which it falls into a tube which may be graduated to read directly in any desired unit, such as ampere-hours, watt-hours or Board of Trade Units. The glass container, after the mercury and the electrolyte have been placed inside, is sealed off. This lessens the chances for change or decomposition of the electrolyte. By inverting the meter for a moment, the mercury from the cathode chamber can be returned to the anode reservoir.

Mercurous perchlorate possesses many properties that make it an ideal salt for use in an electrolytic meter. Mercurous perchlorate is very soluble in water. The ClO_4 radical is absolutely unaffected by electrolysis or any other ordinary treatment except ignition. The slightest indication of any decomposition of the ClO_4 radical has never been detected in any of the many perchlorate baths that have been tried in this laboratory. In addition to mercury, which is described in this paper, lead,[4] silver, tin, copper, indium[5] and other metals have been electrolytically deposited from perchlorate solutions. Aqueous solutions of mercurous perchlorate do not readily hydrolyze nor form basic salts. Mercury anodes corrode and dissolve perfectly in perchlorate baths. Perchloric acid is a strong acid and possesses good electrical conductivity, ranking above nitric acid. Twice as much mercury will be deposited from a mercurous perchlorate bath as from any mercuric bath. This is an added advantage of mercurous perchlorate over potassium mercuric iodide.

Preparation of Materials.

Perchloric acid was made by treating barium perchlorate with an equivalent amount of sulphuric acid. The precipitate of barium sulphate was removed by filtration. The filtrate contain-

[3] Bulletins issued by Schott and Gen.
Hatfield, *loc. cit.*

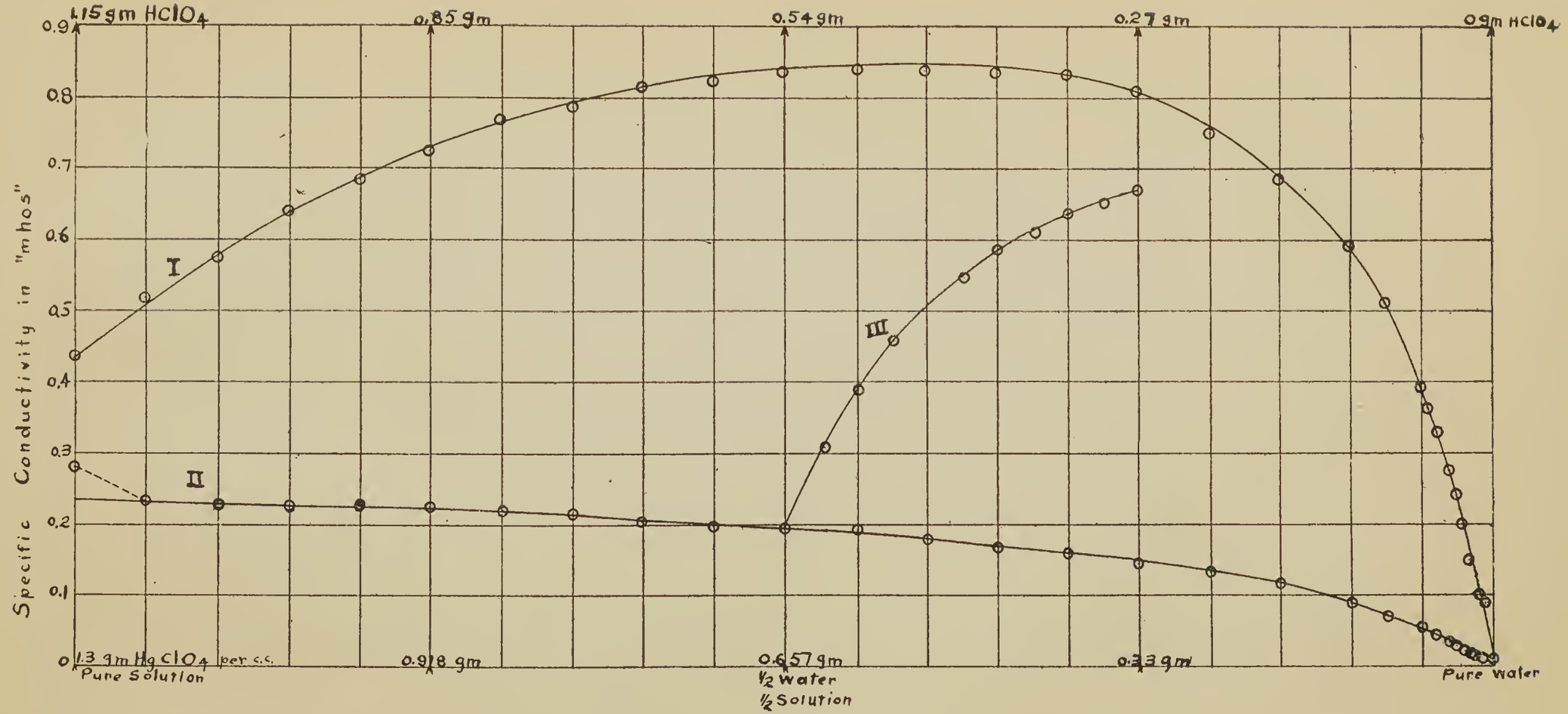
[4] Mathers, Trans. Amer. Electrochem. Soc. **17**, 261 (1910).
Mathers, Chemiker-Zeitung, p. 1316 (1910).

[5] Unpublished details of experiments on indium perchlorate.
Mathers and Schluederberg, Jour. Amer. Chem. Soc., **30**, 211 (1908).

ing the dilute perchloric acid was heated on a hot plate until the temperature reached about 135°-150° C. This treatment volatilized a large part of the water and all of the hydrochloric acid which was an impurity in the barium perchlorate. This solution was then distilled under reduced pressure. The low boiling products were rejected, while the distillate, corresponding to 201°-203° C., was saved. This distillate had the approximate composition $HClO_4.2H_2O$.

The *mercurous perchlorate* which was used in the early experiments in this research was prepared by dissolving freshly precipitated mercurous oxide in perchloric acid. Solutions prepared in this way always gave low results in the coulometer. Analysis showed the presence of small amounts of mercuric mercury. Mercurous oxide is unstable, and easily decomposes in the presence of light into mercuric oxide and metallic mercury.[6] The low values in the coulometer are explained by the fact that mercuric mercury has an electrochemical equivalent of just one-half that of mercurous mercury. Pure mercurous perchlorate was prepared by an electrolytic method. Pure perchloric acid was electrolyzed in a small beaker with mercury in the bottom as anode. A small piece of platinum gauze, reaching just below the surface of the electrolyte, was used as cathode. The solution was stirred occasionally—just enough to break up the layer of crystallized mercurous perchlorate which tended to form upon the surface of the anode. The dense mercurous perchlorate solution remained in the bottom of the beaker on the mercury anode. Hydrogen and only small amounts of mercury were precipitated upon the cathode. As the quantity of mercurous perchlorate increased, the stirring and diffusion brought mercury ions to the cathode in gradually increasing quantities, where they were precipitated. The electrolysis was terminated when large amounts of mercury began to be deposited upon the cathode. Water was added, and the solution was stirred until the mercurous perchlorate crystals went into solution. This solution, after filtration, was ready for use as a coulometer solution. The amount of free acid which was present in the solution thus prepared was about the quantity that was required to make a good coulometer electrolyte.

[6] Erdmann, Lehrbuch anorganischen Chemie, p. 579 (1906).



Concentration of Solutions.

Curve I: $HClO_4 \cdot 2H_2O$ from 0% to 100%

Curve II: $HgClO_4$ from 0% to saturated solution at 40° C.

Curve III: 5 c.c. $HgClO_4$ saturated at 40°C + 5 cc. H_2O, diluted with 50% $HClO_4 \cdot 2H_2O$.

Conductivity Experiments.

A good coulometer solution should have a low electrical resistance; conductivity measurements were therefore made to determine the best conducting solutions of mercurous perchlorate and perchloric acid. The determinations were made at 40° C. by the Kohlrausch method. The data for solutions of perchloric acid and of mercurous perchlorate were taken by starting with solutions of definite strength and by adding 1 c.c. portions of water until 10 c.c. had been added to 10 c.c. of the solution; and *vice versa,* by adding 1 c.c. portions of the solution to 10 c.c. of water until 10 c.c. had been added. Data for the mixture of mercurous perchlorate and perchloric acid were obtained by the use of the above strong solutions, each diluted with an equal volume of water, then 1 c.c. portions of this diluted acid were added to 10 c.c. of the diluted mercurous perchlorate solution until 10 c.c. had been added. The concentration in grams per c.c. is given with the curves and tables which follow:

CONDUCTIVITY DATA.

Solutions of $HClO_4$ 2 H_2O				Solutions of $HgClO_4$.			
c.c. $HClO_4$ 2 H_2O Sol. to 10 c.c. H_2O.		c.c. H_2O to 10 c.c. $HClO_4$ 2 H_2O Sol.		c.c. H_2O to 10 c.c. Sat. (40°C) $HgClO_4$ Sol.		c.c. Sat. (40°C) $HgClO_4$ Sol. to 10 c.c. H_2O.	
c.c. acid	Sp. Cond.=K.	c.c. H_2O.	Sp. Cond.=K.	c.c. H_2O.	Sp. Cond.=K.	c.c. $HgClO_4$	Sp. Cond.=K.
0	10.119×10^{-5}	0	0.4374	0	0.2809	0	10.119×10^{-5}
0.1	0.08708	1	0.5192	1	0.2323	0.1	0.00732
0.2	0.09932	2	0.5811	2	0.2281	0.2	0.01364
0.3	0.15767	3	0.6435	3	0.2281	0.3	0.01935
0.4	0.19984	4	0.6903	4	0.2254	0.4	0.02502
0.5	0.24192	5	0.7307	5	0.2218	0.5	0.03016
0.6	0.27394	6	0.7706	6	0.2182	0.6	0.03462
0.7	0.30521	7	0.7934	7	0.2121	0.7	
0.8	0.3313	8	0.8208	8	0.2037	0.8	0.04455
0.9	0.3669	9	0.8298	9	0.1959	0.9	
1.0	0.3953	10	0.8388	10	0.1915	1.0	0.05272
1.5	0.5136					1.5	0.06935
2	0.5954					2	0.08637
3	0.6900					3	0.1150
4	0.7572					4	0.1350
5	0.8101					5	0.1520
6	0.8354					6	0.1558
7	0.8395					7	0.1672
8	0.8395					8	0.1740
9	0.8395					9	
10	0.8234					10	0.1915

Solutions of $NaClO_4$			Solutions of $HgClO_4 + HClO_4 . 2 H_2O$	
Strength	K. at 38°C	K. at 25.8°C.	c.c. $HClO_4 . 2 H_2O$ (50% Sol.) to 5 c c. H_2O + 5 c.c. $HgClO_4$ Sol. Sat. at 40°C	
			c.c. acid.	Sp. Cond.=K.
N	0.09377	0.08217		
N/2	0.05245	0.04242		
N/4	0.02903	0.02339		
N/8	0.01555	0.01243	0	0.1895
N/16	0.00824	0.006621	1	0.3040
N/32	0.004407	0.003532	2	0.3867
N/64	0.002378	0.001903	3	0.4571
N/128	0.001258	0.001007	4	
			5	0.5445
			6	0.5829
			7	0.6106
			8	0.6402
			9	0.6557
			10	0.6718

The conductivities of perchloric acid given are the averages of several readings at different points on the bridge wire. The other readings were taken as near the center of the bridge wire as possible. The cell constant ranged from about 0.25 to 0.28, so that in the case of high conductivities the readings had to be made some distance from the middle of the bridge wire.

The data and curves show that:

1. A solution of perchloric acid containing 0.43 grams per c.c. has maximum conductivity. (Curve I.)

2. The conductivity of mercurous perchlorate increases slowly with increase in concentration. (Curve II.)

3. The conductivity of solutions of mercurous perchlorate increases very rapidly with increasing amounts of free perchloric acid. (Curve III.)

Coulometer Experiments.

At the time when these experiments were performed the glass part of a meter such as Schott and Gen. is manufacturing could not be obtained, so another form of apparatus was devised. Iridium foil is said to be used as cathode in the Stia meter. Perhaps an iridium-platinum alloy or iridium plated upon platinum was meant. Pure iridium is brittle[7] and cannot be made into foil. The cathode must be of some material that is insoluble in the electrolyte and which does not form an amalgam with mercury. Tantalum is also mentioned as suitable material for a cathode. Magnetic oxide of iron was tried, but it cannot

[7] Erdmann, *loc. cit.*, p. 728.

be used because it is gradually disintegrated with formation of a fine black powder which becomes mixed with the deposited mercury. Palladium and platinum easily amalgamate with the mercury. An apparatus that allowed the use of a mercury cathode was finally arranged as follows:

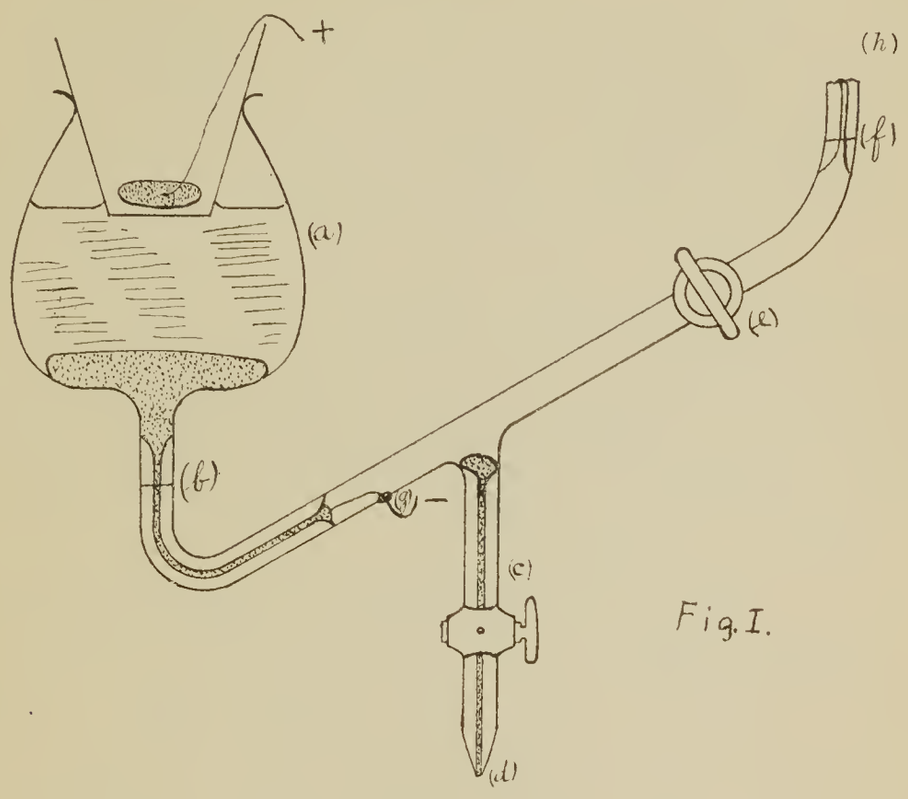


Fig. I.

Fig. 1 shows the form of the cell that was employed. The end of a large thistle tube (a) was sealed to a capillary tube of about 0.6 mm. bore. To this was sealed a tube of larger diameter (3 to 4 mm.) containing a stop-cock (e) and bearing a side-arm capillary delivery tube with stop-cock (c). At the end of the large bore tube another capillary tube (h) was sealed. The marks (b and f) were made upon the capillary tubes with hydrofluoric acid. The purpose of the large-bore tube was to serve as a convenient reservoir for the constant excess of mercury that was required for cathode material. Connection was made to the cathode by means of a platinum wire which was sealed into the tube at (g). The anode cell used in these experiments was a Gooch crucible, containing a layer of glass wool, upon which rested from 20 to 30 grams of mercury, which served as anode. This crucible was placed in the thistle tube so that it was partially immersed in the electrolyte. This arrangement of

the electrodes provided for a very efficient and convenient stirring of the electrolyte. The heavy liquid falling from the anode mixed with the light liquid rising from the cathode and thus the electrolyte was thoroughly stirred. At no time was any mechanical stirring or mixing required.

At the beginning of an experiment the cell was filled with mercury between the marks (b) and (f). The mercury was then forced into the thistle tube by means of a rubber bulb attached at (h), enough being left in the reservoir to make a good electrical connection with the negative terminal wire, and the stop-cock (e) was closed. At the termination of an experiment the mercury was allowed to flow back until it reached the mark (f), and the stop-cock (e) was turned off. The excess of mercury above the graduation (b) was run out through stop-cock (c) into a beaker to be weighed, or into specially prepared graduated tubes for measurement. The data from a number of experiments are given in the following tables:

Hg and Cu Coulometers in Series.

Exp. No.	Current	Current Density A per sq.dm.		Wt. Cu Deposited	Wt Hg Deposited	Hg Calculated From Cu	Per Cent. Error	Remarks
		Anode	Cathode					
	amp.			grm.	grm.	grm.		
3	0.135	4.18	1.89	0.3068	1.9386	1.9302	+0.43	In Nos. 3-6 the deposited Hg was measured in a graduated capillary tube
4	0.135	4.18	1.89	0.2207	1.3813	1.3880	—0.48	
5	0.410	12.71	5.79	0.3221	2.0180	2.0258	—0.38	
6	0.55	17.05	7.70	0.4935	3.1000	3.1037	—0.12	
7	0.85	26.35	11.90	1.0457	6.5578	6.5767	—0.28	
8	1.60	49.60	22.40	1.7712	11.0818	11.1396	—0.52	
9	2.30	71.30	32.20	1.4427	9.1225	9.0736	+0.52	Electrolyte warm
10	3.10	96.10	43.40	1.6545	10.4013	10.4056	—0.04	" very warm
11	0.20	6.20	2.80	0.4936	3.1075	3.1044	+0.10	
12A	0.50	15.50	7.00	1.4220	8.9808	8.9421	+0.40	
12B	0.50	15.50	7.00	1.4220	8.9700	8.9434	+0.30	
13B	0.85	26.35	11.90	1.4936	9.4348	9.3937	+0.43	
14A	0.50	15.50	7.00	1.2227	7.6707	7.6899	—0.25	
14B	0.50	15.50	7.00	1.2227	7.6908	7.6899	+0.01	

Hg, Cu and Ag Coulometers in Series.

Ex.p. No.	Current	Wt. Ag. Deposited	Wt. Cu. Deposited	Wt. Cu. Calculated from Ag.	Per Cent. Error	Wt. Hg. Deposited	Wt Hg. Calculated from Ag.	Per Cent. Error
	(amp.)	(grm.)	(grm.)	(grm.)		(grm.)	(grm.)	
13 B.	0.85	5.0711	1.4936	1.4941	—0.03	9.4348	9.3970	+0.40
14 A.	0.50	4.1451	1.2227	1.2213	+0.11	7.6707	7.7003	—0.38
14 B.	0.50	4.1451	1.2227	1.2213	+0.11	7.6908	7.7003	—0.12

The conditions for the above experiments were:

Anode area, about 3.14 sq. cm.

Cathode area, about 7 sq. cm.

Distance between the anode and cathode, about 2.5 cm.

Volume of the electrolyte, about 35 c.c.

The composition of the electrolyte was: 0.642 gram of $HgClO_4$ per c.c., 0.2836 gram of $HClO_4$ per c.c. and 0.04 gram of $NaClO_4$ per c.c. In some early experiments the mercury was deposited in a finely-divided black condition. The addition of small amounts of sodium perchlorate to the electrolyte seemed to overcome this difficulty.

Changes in temperature during the course of the experiments affect the accuracy of the results. The electrolyte should be at the same temperature when readings are taken before and after electrolysis. When the electrolyte is heated by the current, the mercury should be allowed to regain its original temperature before it is drawn off. A correction could be applied for the thermal expansion of the mercury in the reservoir. This would eliminate the trouble in obtaining the original temperature.

Summary.

These preliminary experiments have shown that mercurous perchlorate solution is a satisfactory electrolyte for a mercury coulometer or meter.

The advantages of mercurous perchlorate solution as an electrolyte for meters and coulometers are:

1. The ClO_4 radical is exceptionally stable and is absolutely unchanged by electrolysis.

2. Mercurous perchlorate is very soluble in water, and the solutions thus formed are entirely free from any decomposition.

3. Mercurous perchlorate solutions containing free perchloric acid have very high conductivity, so that a very high current density may be used in electrolysis.

4. The amount of mercury deposited may be very rapidly determined by measurement rather than by the much slower method of weighing.

5. The deposited metal is in such form that it may be transferred to the anode for further use without any treatment whatever.

6. Equivalent quantities of electricity deposit from two to six times greater weight of mercury(ous) than of the other metals. This gives greater accuracy.

University of Indiana.
Bloomington, Indiana.

DISCUSSION.

MR. C. G. SCHLUEDERBERG: As regards chemical meters, they have not, up to date, been popular in this country. There has been, and, in fact, still is, considerable prejudice against them, and they are practically not used here. Chemical meters are used to some extent in Europe, and, I believe, with a fair degree of success for the smaller installations, such as ordinary house lighting, where but a moderate amount of current is required to be metered.

In this country, alternating current has come to be used for a large majority of the house lighting and power service. For the measuring of this current the induction type of meter has been developed to a point where it is so satisfactory that it is questionable whether any other type of meter will ever be adopted.

The mercury type of meter is, of course, adapted for use on direct current circuits only, and for smaller installations, where the amount of current to be metered is comparatively small. It is impracticable to make a mercury meter of a size suitable for carrying very large current, although this criticism may be objected to on the ground that it is possible to use an ordinary shunt. In an ordinary shunt the highest drop that would commonly be used is 50 or perhaps 100 millivolts, and this is hardly sufficient for the successful operation of a chemical meter.

As far as the question of accuracy is concerned, this meter of Dr. Mathers is plenty good enough, as it is within one-half of one percent plus or minus. The ordinary guarantees on the commercial induction meter are two percent, plus or minus,

though most of them are, of course, considerably more accurate.

As I have said, there is a great deal of prejudice in this country against chemical meters, which would have to be overcome, and, in addition, meters of this type are subject to temperature errors, and, furthermore, they freeze in winter—a very serious objection. They must be read once every so often, otherwise the tube containing the mercury will fill up and the meter cease to register, while the ordinary induction type of meter can go on until the dial has registered a complete cycle, which requires a long time, and after that the meter repeats itself. Furthermore, the chemical meter has to be handled with a great deal of care, while the induction meter can be handled by any lineman with entire success.

The chemical meter would give one advantage, and that is its cheapness in first cost. I imagine one of these meters could be sold for $3.00 or $4.00 as against $10.00, which is approximately the price of the ordinary house type of induction meter.

MR. CARL HERING: It was originally said in the discussion that if a shunt is used, it would involve a greater drop. The drop around the cell is the same whether you shunt it or not. A shunt would not increase the drop.

MR. SCHLUEDERBERG: I meant that any type of commercial shunt must not have too great a drop; in other words, in ordinary service one would not care to use a shunt having over 100 millivolts drop, and that amount would hardly be satisfactory for meter operation.

MR. HERING: If the drop in the cell is too high, then the drop of the shunted meter will be too high also.

DR. CLAYTON H. SHARP: Is not that a question of the accuracy of the meter under temperature changes? The meter itself would have a negative temperature coefficient, and the shunt having a zero temperature coefficient, certainly not a negative temperature coefficient, the two would fail to compensate for the temperature difference, so that it would be necessary to have a shunt with a pretty large drop and a series resistance of positive temperature coefficient in order to compensate for the temperature changes.

In speaking of the electrolytic meter, there is one disadvantage

which has not been mentioned, and that is that the electrolytic meter is so constructed that it leaves no record of its past performance,—that is, a meter reader reads it, and he destroys the record entirely by putting the recording device back. The ordinary meter retains the record continuously, so that if a mistake is made it is adjusted on the next month's bill.

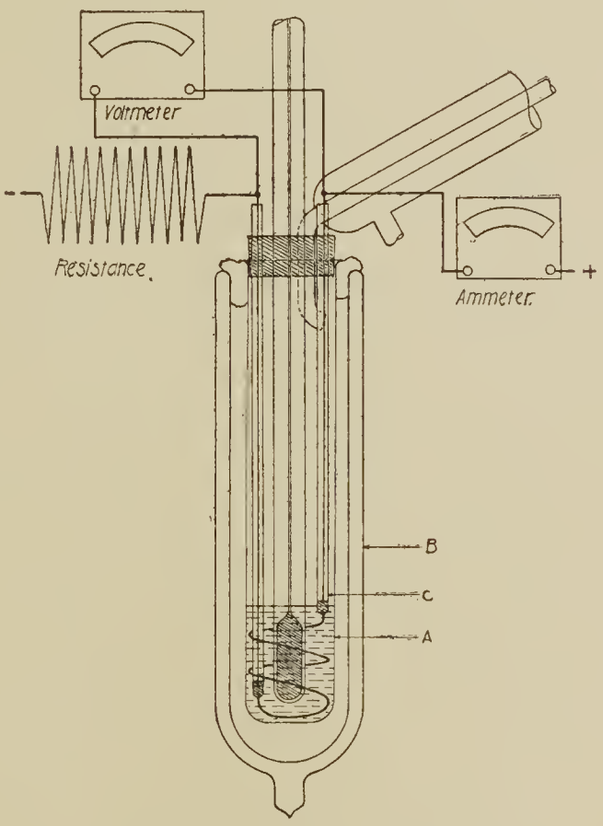
Dr. F. C. Mathers (*Communicated*): The "Stia" meter seems to avoid many of the difficulties and objections that have been mentioned in these discussions. For example, the glass parts of the meter may be constructed so that the first reading tube, when full of mercury, will be emptied automatically by a siphon into a tube of large diameter. This large tube may be graduated in units that are ten or even one hundred times that of the smaller tube. By this means, the record of the performance of the meter is retained. Such a meter will record continuously until the quantity of mercury in the anode reservoir is exhausted.

A paper read at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 7, 1911, President Wm. H. Walker in the Chair.

ELECTRICAL HEATING AS A MEANS OF PREVENTION OF SUPERHEATING OF LIQUIDS

By J. Howard Mathews.

For the past three years a modification of the ebullioscopic method for determining molecular weights, in which the heat is supplied electrically,[1] has been used in this laboratory with very satisfactory results. The method has proven to be far superior to the cumbersome method of heating with a gas flame, with its mantles, glass beads, agates or platinum tetrahedra and other devices of equally doubtful merit.



As used in our laboratory, the apparatus consists of a boiling chamber, 4 by 20 cm., closed by a cork stopper, through which pass the Beckmann thermometer, return tube from the condenser

[1] Bigelow. Amer. Chem. Jour. **22**, 280 (1899).
Beckmann. Zeitschr. phys. Chem. **63**, 184 (1908).

and the two small glass tubes containing the wires through which the current is led to the platinum heating spiral. The ends of the wire are sealed into the glass tubes by means of fusible glass. The boiling tube is entirely enveloped within an un-silvered Dewar cylinder. Circulation of air between boiling chamber and the vacuum jacket is prevented by a rubber gasket or by cotton.

The essential difference between our method and that recommended by Bigelow and by Beckmann consists in the disposition of the heating wire. Both of these investigators formed the platinum wire into a closely coiled spiral, which was placed underneath the thermometer. We have found it a great advantage to make the wire into a large vertical coil of large diameter, as shown in the figure. The bulb of the thermometer is placed in the center of the coil. Bubbles of vapor, in rising, do not touch the thermometer, but rise directly to the surface of the liquid. The vortex motion thus produced is exceedingly effective in stirring the liquid; in fact, it is much more so than when the coil is placed below the thermometer in one horizontal plane.

It has also been found advantageous to flatten off the bottom of the boiling tube in order that the coil may extend practically to the bottom. When the coil is not so placed, the liquid at the bottom is not stirred as effectually, layers of more or less stagnant liquid forming, with a resulting inequality of temperature. With the flat bottom this difficulty disappears.

Another decided departure from the method as used by Bigelow and Beckmann consists in the use of stronger electric currents. It has been our experience that much less superheating results when fairly heavy currents are sent through a comparatively short and heavy wire. Our heating elements usually consist of two strands of No. 26 (0.38 mm.) platinum wire, of about 20 cm. in length, twisted together and coiled as described, through which a current of from 10 to 14 amperes is passed. With such a heating element, far less superheating is experienced than with a coil made from a long, fine wire, through which a current of low amperage is passed. This point has been tested and confirmed repeatedly.

The current is maintained at constant strength by means of a suitable rheostat with sliding contact. Inasmuch as constancy of boiling point is highly dependent upon the constancy of the

rate at which the condensed and cooled liquid returns from the condenser, it is very necessary that heat be supplied at a perfectly fixed rate. Naturally such accurate control is all the more necessary when large currents are sent through small resistances, but this is a requirement easily satisfied, and constitutes no objection to the use of the heavier currents.

The condensed liquid drops freely from the condenser to the violently agitated boiling liquid below. Fluctuations in temperature always result if the liquid runs down the thermometer, the outside walls or the glass tubes, these fluctuations being due to imperfect mixing.

Austin[3] has shown that the heat transfer resistance between a metal surface and a liquid is highly dependent upon the agitation of the liquid. This is true even in the case of boiling liquids. He found that by rapid mechanical stirring of boiling water, the transfer resistance could be reduced over 25 percent. He also ascertained that with constant stirring the heat transfer is proportional to the difference in temperature between metallic surface and liquid. In this same connection, Rogovsky[4] has found that the temperature of a silver wire, immersed in water and carrying a current, may be as much as 25° C. higher than the temperature of the water with which it is in contact. This shows that the heat transfer resistance may be very great indeed.

It has been shown by several investigators that the transfer resistance between a metal and water in contact with it suddenly diminishes very considerably at the moment that ebullition begins, and it has been suggested that the increased absorptive power of water for heat at that point might be due to a change in the nature of the water. The experiments of Halliday,[5] however, show that the increased absorption of heat at the point of ebullition is due to the increased circulation produced, and to this alone.

Austin points out that if this transfer resistance is due to a film of water adhering to the metal, it is natural to suppose that the thickness of the film is dependent upon the condition of the surface of the metal; but he found no difference when the surface was greasy and dirty. Neither was any difference produced when the water contained rust in suspension. In this same connection,

[3] Zeitschr. ver. Deutsch. Ing. **46**, 1890 (1902).
[4] Comptes rendus, **137**, 1244.
[5] Engineer. **87**, 473 (1899).

Hausbrand[6] states that the nature of the metal of which a heating surface is composed appears to affect the amount of heat transference only through differences in heat conductivity of the metal itself, and, furthermore, that the nature of the surface, whether rough or smooth, seems to be entirely without influence on the movement of heat.

On the other hand, Blechynden,[7] from measurements made to determine the transmission powers of copper and iron plates to conduct heat from hot gases on one side to water on the other, found that they were about equal in this respect, but that the iron, if new and bright, transmitted heat rather better than copper. Blechynden's work has been repeated at the German Reichsanstalt, and his results have been confirmed. It was also found that the thickness of the metal plates used was practically immaterial, but that the condition of the surface had some effect, due to a change in the radiation power only.

Experiments made by Carpenter,[8] in which plates of cast iron were pickled in nitric acid for different lengths of time, showed that the heat transmission became poorer the longer the plate was pickled. Since cast iron is an in-homogeneous substance, containing a substance of relatively poor thermal conductivity, this result was to have been expected.

Stirring of the liquid seems to serve two purposes—to secure uniformity of temperature by complete admixture, and to break up or make thinner the film that causes the transfer resistance. Austin tried to remove this film with revolving brushes, but failed. It is evident, however, that stirring of the boiling liquid does produce beneficial results, and it is obvious that the rapid circulation of the liquid, caused by the entraining action of the vapor, when boiled by heavy currents should lessen the tendency to superheat, and such is found to be the case. Less superheating is always experienced when the liquid boils at a lively rate. The necessity of rapid boiling has also been pointed out by Beckmann.[9] Undoubtedly part of the beneficial effect is to be attributed to the cooling action of the larger quantity of condensed and cooled liquid returning from the condenser.

[6] Evap. and Condens. App.
[7] Engineer (London) 509, (1896).
[8] Trans. A. S. M. E. 12, 179.
[9] Zeitschr. phys. Chem. 40, 134, 140, 156 (1902).

If complete circulation of the boiling liquid is essential, it would seem that the use of glass beads or other material packed around the bulb of the thermometer, for the purpose of breaking up the bubbles of vapor, would be more of a disadvantage than an advantage, and this conclusion is fully confirmed by the following experiment:

The apparatus was set up as described (with a platinum wire for the heating element), and contained 50 c.c. of re-distilled carbon tetra-chloride. This substance was chosen in this and the experiments following for the reason that it is a liquid which, on account of its low specific heat and high density, superheats readily. After the liquid had been boiling for several minutes and sufficient time had elapsed for the different parts to assume thermal equilibrium, simultaneous readings of temperature, current and barometric pressure were taken at intervals of exactly one minute for a considerable period. Three series of readings were taken, the current strength being different in each.

Then, without dismantling the apparatus or disturbing the disposition of the various parts in any way, glass beads of an average diameter of 3 mm. were introduced into the boiling liquid through the condenser until the heating coil and bulb of the thermometer were covered. Again three series of readings were taken, using the same current strengths as before. Table I shows the results obtained, and demonstrates very clearly the disadvantage of using the beads.

TABLE I.

Amperage	Bar. Pressure (mm.)	Duration of Test (Min.)	Average Temp. of Boiling C°	Maximum Variations, + and —, from the mean temp.
WITHOUT BEADS				
10	739.4	26	1.861°	—0.004° +0.004
7	733.0	27	1.698	—0.006° +0.005
WITH BEADS				
10	733.0	28	1.900°	—0.016° +0.010
7	733.0	26	1.880°	—0.033° +0.022

It will be noted that the fluctuations in temperature were from four to five times greater when the beads were used, and that the temperatures at which boiling took place were higher. The

fluctuations in temperature are obviously due to imperfect circulation and the slow transmission of heat through the poorly conducting glass beads. The fact that the temperature of boiling was higher with the beads was due to local superheating and the slow mixing of the condensed and cooled liquid returning from the condenser. In molecular weight determinations this effect would naturally be all the more pronounced, for the concentration of the solution would not be uniform—that at the top being more dilute—and consequently a considerable error might be introduced.

With the apparatus as described, and with the precautions enumerated, it has been found possible to determine molecular weights in solution with a degree of accuracy heretofore unattainable. However, in spite of the application of all of these preventive measures, a small superheating effect is often experienced. This generally amounts to less than 0.01°, but even so small a degree of superheating is often undesirable.

The question arose as to whether the same extent of superheating would be experienced when the heating element was composed of some other material than platinum. Preliminary experiments made a year ago by Mr. L. I. Shaw, of this laboratory, at the suggestion of the writer, seemed to show that with Monel resistance wire the superheating effect was greater than with platinum. The writer has since extended these tests to heating elements composed of German silver and the resistance wires known as Monel, Ni-chrome, Advance and Manganin.

In these tests, wires of approximately the same diameter were chosen. The heating element consisted of two strands of wire, twisted together to give the coil more rigidity, in the form of a large open coil having two and one-half turns. The wires were about 20 cm. in length in each instance, and great care was taken to have the size and position of the coil the same in all the experiments. Because of the small differences in size and length, and differences in the electrical resistance of the different wires used, several series of readings (with varying strengths of current) were taken for each heating element.

The results of these experiments are summarized in the following table. To save space, the enormous number of individual readings, taken every minute, are not given. During each

series the strength of current was maintained at exactly the figure indicated.

TABLE II.

Platinum Wire.

Diameter = 0.381 mm. Length = 195 mm. Resistance at B. P. = 0.226 ohm.

Current (Amp.)	Duration of test (Min.)	Bar. Press. (mm.)	Average Temperature C°	Maximum variations in temperature + and —.
13.0	26	733.0	1.656°	—0.003° +0.001
11.5	34	738.1	1.840°	—0.007 +0.003
10.0	26	739.4	1.861	—0.004 +0.004
8.5	35	740.9	1.898	—0.005 +0.008
7.0	28	733.2	1.699	—0.007 +0.004

German Silver Wire.

Diameter = 0.419 mm. Length = 205 mm. Resistance at B. P. = 0.251 ohm.

10.0	38	740.1	1.911	—0.015 +0.014
8.5	22	739.7	1,982	—0.022 +0.016

Ni-chrome Wire.

Diameter = 0.406 mm. Length = 200 mm. Resistance at B. P. = 0.969 ohm.

7.0	24	749.7	2.231	—0.004 +0.002
5.5	23	750.2	2.243	—0.003 +0.005

Advance Wire.

Diameter = 0.457 mm. Length = 195 mm. Resistance at B. P. = 0.342 ohm.

11.5	12	742.2	2.102	—0.002 +0.002
10.0	29	738.4	1.890	—0.003 +0.003
8.5	27	738.4	1.940	—0.002 +0.006

Monel Wire.

Diameter = 0.406 mm. Length = 190 mm. Resistance at B. P. = 0.442 ohm.

10.0	21	746.1	2.226°	—0.002° +0.002
8.5	48	746.1	2.256	—0.007 +0.007
5.5	37	746.1	2.366	—0.006 +0.007

Manganin Wire.

Diameter = 0.419 mm.		Length = 190 mm.	Resistance at B. P. = 0.330 ohm.	
10.0	25	733.7	1.783	—0.004 +0.006
8.5	38	733.1	1.803	—0.004 +0.005

Naturally the choice of giving *maximum* fluctuations instead of average fluctuations from the mean temperature serves to exaggerate the superheating effect somewhat, since in a number of cases all but a very few of the individual readings were practically identical.

The results show conclusively that we are by no means limited to the use of platinum wire for the construction of heating elements where superheating of non-corroding liquids is to be avoided. The Ni-chrome and Advance resistance wires are particularly suitable for such purposes. The sample of Ni-chrome wire used was covered with oxide when obtained, and was cleaned with very fine emery powder dusted on a cloth. The other wires were clean and bright, and were not so treated. It is likely, as will be shown later, that this treatment improved the non-superheating qualities of the wire by roughening the surface. The Ni-chrome wire was the only one which blackened upon use. The others remained perfectly bright.

German silver caused a much larger superheating effect than any of the other wires used.[10] The test was repeated, using one strand of larger wire in place of the two small ones. Three series of readings with different strengths of current confirmed the result of the earlier test. The wire was then oxidized by heating, and another series of readings taken to determine whether the superheating effect would be modified by the presence of the layer of oxide. The oxide seemed to produce little or no effect.

Tests were then made to ascertain whether wire of the same size rolled out into the form of a thin ribbon would cause the same superheating effect as the round wire. It was thought that by so increasing the area of the heat dissipating surface, superheating might be reduced. A piece of No. 22 wire, the size used in the last test, was rolled into a ribbon, the approximate dimensions of which were 205 mm. in length, 1.22 mm. in width

and 0.25 mm. in thickness. Experiments made with this form of resistance wire showed some improvement. The same wire was then well roughened by scratching with a file, and three series of readings taken. It was found that roughening of the heat dissipating surface had a very beneficial effect. In fact, the so roughened wire of German silver produces about as little superheating as any of those used, as is shown clearly in Table III.

TABLE III.

German Silver Wire.

Current (Amp.)	Duration of test (min.)	Bar. Press. (mm.)	Average Temperature	Maximum variations + and —.
1....10.0	36	732.5	2.449°	—0.019° +0.026
2.... 7.5	12	732.5	2.588	—0.011 +0.018
3.... 7.5	21	732.5	2.493	— .016 +0.015
4....10.0	30	740.7	2.752	—0.006 +0.007
5.... 8.5	31	741.7	2.933	—0.008 +0.008
6....10.0	30	734.8	2.622	—0.005 +0.005
7.... 8.5	12	734.8	2.623	—0.002 +0.002
8.... 7.5	30	734.7	2.629	—0.004 +0.003

In 1 and 2 the wire was 0.660 mm. in diam., 230 mm. in length and had a resistance of 0.263 at B. P.

In 3 the wire was of same dimensions as in 1 and 2, but was oxidized.

In 4 and 5 wire of same size was rolled into ribbon. Length = 200 mm. Resistance = 0.258 ohms. at B. P.

In 6, 7 and 8 the ribbon was well roughened with a file. Resistance = 0.258 ohms. at B. P.

Conclusions.

It has been shown that the degree of superheating of a liquid boiled by the heat generated by an electric current passing through a resistance wire in it is dependent to some extent upon the nature of the wire, but that it is much more highly dependent upon the condition of the surface. The bubbles of vapor form on inequalities of the surface, and the greater the number of

[10] It is interesting to note that H. S. Bailey (Jour. Am. Chem. Soc. **33**, 447 (1911), who has recently devised an apparatus for fractional distillation in which electrical heating is used as suggested by Richards and the writer (Jour. Am. Chem. Soc. **30**, 1283; **31**, 1200) states that German silver produces less superheating than platinum. This is evidently an erroneous conclusion.

these, the more points will there be at which bubbles can form. Increase in the number of bubbles formed decreases the tendency to superheat. Increase in the rate of boiling, so that more perfect circulation and mixing of the liquid are produced, results in a decrease in the superheating effect.

Laboratory of Physical Chemistry,
University of Wisconsin,
March, 1911.

DISCUSSION.

PROF. H. K. RICHARDSON: Has Dr. Mathews used platinum black?

DR. J. H. MATHEWS: I have not tried any other materials than those described. It might be a good thing to use. I also intend to try iron wire.

A paper presented at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 7, 1911, President Wm. H. Walker in the Chair.

POLARIZATION IN ITS RELATION TO THE DECOMPOSITION PRESSURE OF ELECTROLYTES.

By Oliver P. Watts.

One of the properties which distinguishes electrolytic from metallic conductors is the relation between the impressed electromotive force and the current which is produced thereby. In a metallic wire, the resistance of which is known, the current may be calculated by an application of Ohm's law. This is not so for electrolytes when "direct current" is used, except for a few combinations of special electrodes and a particular electrolyte.

If a gradually increasing E. M. F. is applied to the ends of a wire and simultaneous readings of the current and pressure are made, the current increases in the same ratio as the E. M. F.

When an electrolytic conductor with electrodes of platinum, carbon, or some other material, insoluble in the particular electrolyte chosen, is substituted for the wire, it is found that for small values of pressure no permanent current flows. The E. M. F. must exceed a certain minimum value before a permanent current is obtained. This minimum value is the so-called decomposition pressure.

In Table I are given the values of current corresponding to the indicated E. M. F. applied to two feet of No. 26 "ni-chrome" wire.

Table I.

Impressed E. M. F. Volts	Current Milli-amperes	Impressed E. M. F. Volts	Current Milli-amperes
0.25	48	1.75	344
.50	95	2.	390
.75	143	2.50	490
1.00	190	3.	586
1.25	242	3.50	680
1.50	292	4.	775

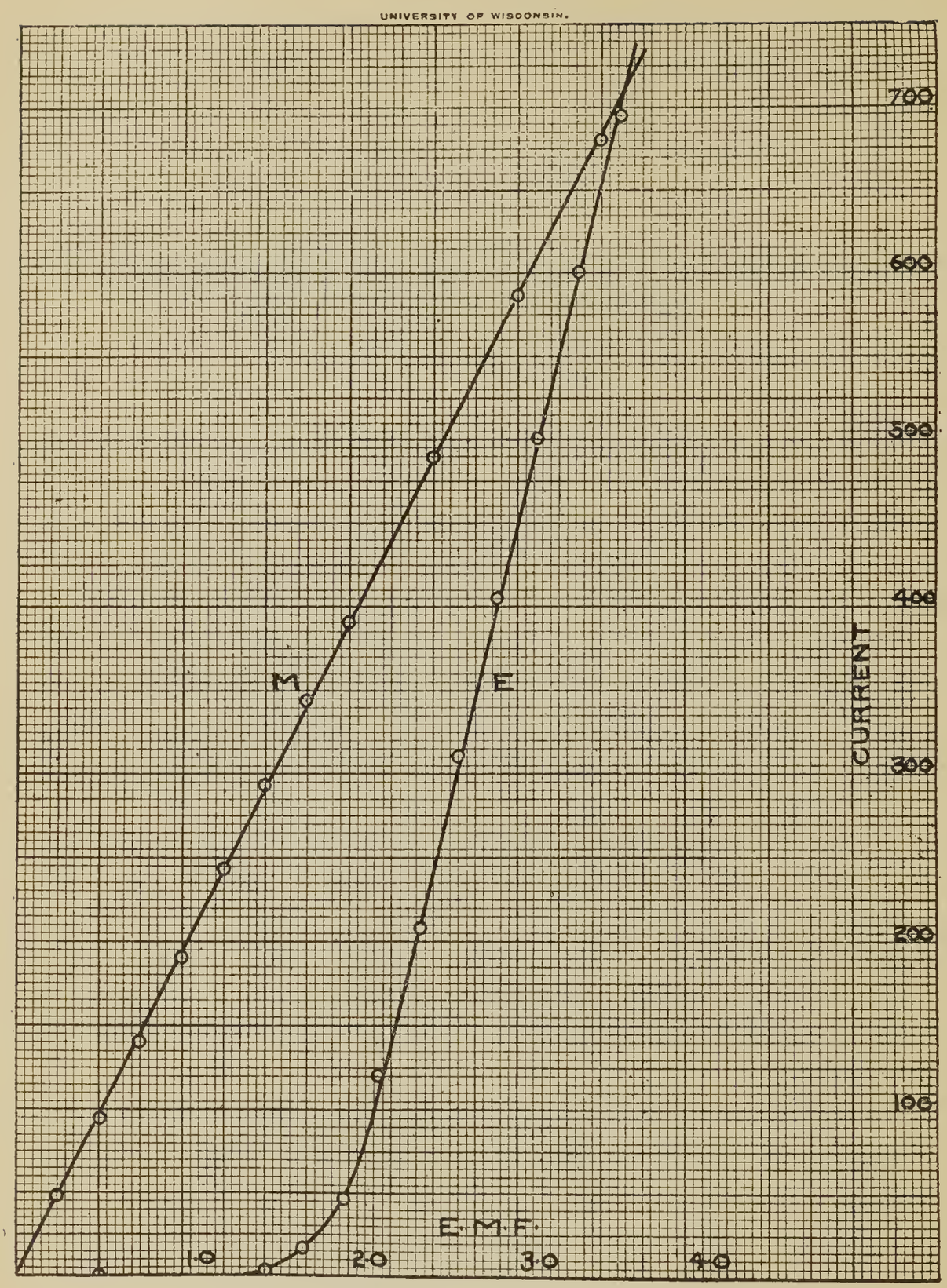


FIG. 1. Current-E. M. F. Curves for a Metallic (M) and for an Electrolytic (E) Conductor.

Figure I shows graphically the relation between current and E. M. F. for the wire, and for a 10 percent solution of zinc bromide with carbon electrodes. The numerical data for the latter are given in Table VI.

It is of interest to review the explanations which have been offered for this peculiar behavior of electrolytes. First in point of time was Grotthus' hypothesis, which was proposed in 1820. According to this, the reason why any pressure, however small, does not send a current through an electrolyte as it does through a metal is because a definite E. M. F. is required to break up the molecules of each particular compound, and therefore no current can pass below that E. M. F. These "decomposition pressures" have been determined experimentally for many different solutions, and it has been found that the more stable a chemical compound is, the greater its decomposition pressure. From the values of the heats of formation and of solution of compounds, it has been found possible to compute values for the decomposition pressures, which agree closely with those obtained experimentally.

Into this seemingly satisfactory agreement of theory with experimental observation, there was projected a disturbing fact. It is possible for an E. M. F. far below the decomposition pressure to produce a considerable momentary current, or a very minute steady current in an electrolyte. To harmonize theory and fact, Clausius, in 1856, suggested that the molecules of a dissolved compound which is capable of conducting an electric current are not firmly locked together, but that the atoms are continually changing partners with their neighbors, and that the E. M. F. is not called upon to disrupt molecules, but only to give direction to the movements of the atoms or radicals during their moments of freedom. It should thus be possible for any E. M. F., however small, to produce a flow of current in an electrolyte.

In the more recent theory of "electrolytic dissociation," advanced by Arrhenius in 1887, it is assumed that by the mere act of dissolving, a large proportion of the molecules of all dissolved substances which yield conducting solutions are broken up into two or more parts.

Thus each of the later theories of the mechanism of the process of electrolysis has been formulated in such a way as to eliminate any "decomposition pressure," yet in every case of electrolysis with insoluble electrodes no permanent current of any magnitude is obtained until a certain voltage has been exceeded. Theoretically the phenomenon of the decomposition pressure has been eliminated; practically, it is still with us.

Although the cause of this phenomenon has been clearly set forth in some of the texts on electrochemistry, there still seems to be considerable misapprehension upon this point.

One view of the cause of the different behavior of metallic and of electrolytic conductors is indicated in the two following quotations:

[1] "The advantages of soluble anodes over insoluble anodes is that a very much smaller E. M. F. is required to produce the same result. * * * This is due in the two cases to a difference in the contact resistance to the current, as it leaves the electrode and enters the solution, which is sometimes called "transfer resistance." This is undoubtedly a physical effect, which must not be confounded with the phenomena of polarization. With insoluble anodes, *this resistance is said to be largely due to a condensed film of gas,* which is only slightly removed by agitation of the liquid, but it is also accounted for by other actions of a more complex nature."

In a very valuable and suggestive paper[2] upon the corrosion of metals, it is pointed out that the rusting and corrosion of iron is an electrolytic process and that the speed of rusting depends upon the rate of removal of a protective film of hydrogen which forms upon the metal. Thus we find:

"One fact regarding the corrosion of iron appears to be undisputed, *viz.,* that oxygen is necessary for a continued action. This corrosive action can cease from two causes, viz., * * * or the action may be stopped by a film of molecular or gaseous hydrogen upon the metal, which, owing to its resistance, prevents the flow of an appreciable current."

It is the purposes of this paper to show clearly that the principal factor in causing the phenomenon of the decomposition voltage as observed in electrolysis is not the *resistance* of a gas or other film upon either or both electrodes, but that it is due to a counter-electromotive force which is produced at the electrodes as a result of the action of the impressed E. M. F. This counter-E. M. F. will hereafter be referred to as polarization.

Let a voltmeter and a milli-ammeter be suitably connected to two platinum electrodes immersed in dilute sulphuric acid or

[1] Cyaniding of Gold and Silver Ores. Julian and Smart, p. 137.
[2] Tr. Amer. Electrochem. Soc., 14, 179 (1908).

sodium chloride, and readings of current made as the impressed E. M. F. is increased. If the circuit is opened from time to time for the purpose of reading the polarization, great difficulty will be experienced, if it be not found utterly impossible, to get satisfactory readings when the electrodes are the small ones of one or two square centimeters area, such as are commonly used for these experiments in the laboratory. The polarization is there, but the voltmeter requires a greater current for its action than this tiny storage cell can furnish.

TABLE II.

Electrolyte, Normal NaCl. Electrodes, carbon.

Impressed E. M F. Volts	Current Milti-amperes	Polarization Volts
0.1	0	0.075
0.2	0	.16
.45	0	.40
.62	0	.58
.84	0	.80
.96	0.25	.88
1.09	0.25	1.03
1.26	0.4	1.18
1.51	1.0	1.38
1.96	5.	1.57
2.21	10.5	1.80
2.51	22.	1.84
2.80	60.	1.84
3.00	105.	1.83

In Table II and Fig. 2 are given the results obtained when the potentiometer is substituted for the voltmeter. The electrolyte was normal sodium chloride and the electrodes were of carbon, 6 x 9 mm., immersed about 37 mm. The curves indicate the reason for no permanent current up to 1.5 volts. With each increase of applied pressure there is developed a counter-electromotive force equal to it, so that no current can flow, and the only reason there is ever any permanent current through an electrolyte when using insoluble electrodes is because there is a limit beyond which the polarization no longer increases in the same ratio as the impressed E. M. F. At about 1.5 volts the polarization lags behind the impressed E. M. F., and at this point the flow of current begins. At about 2.5 volts the polarization has reached its maximum value, so beyond this pressure the current varies directly as the impressed E. M. F.

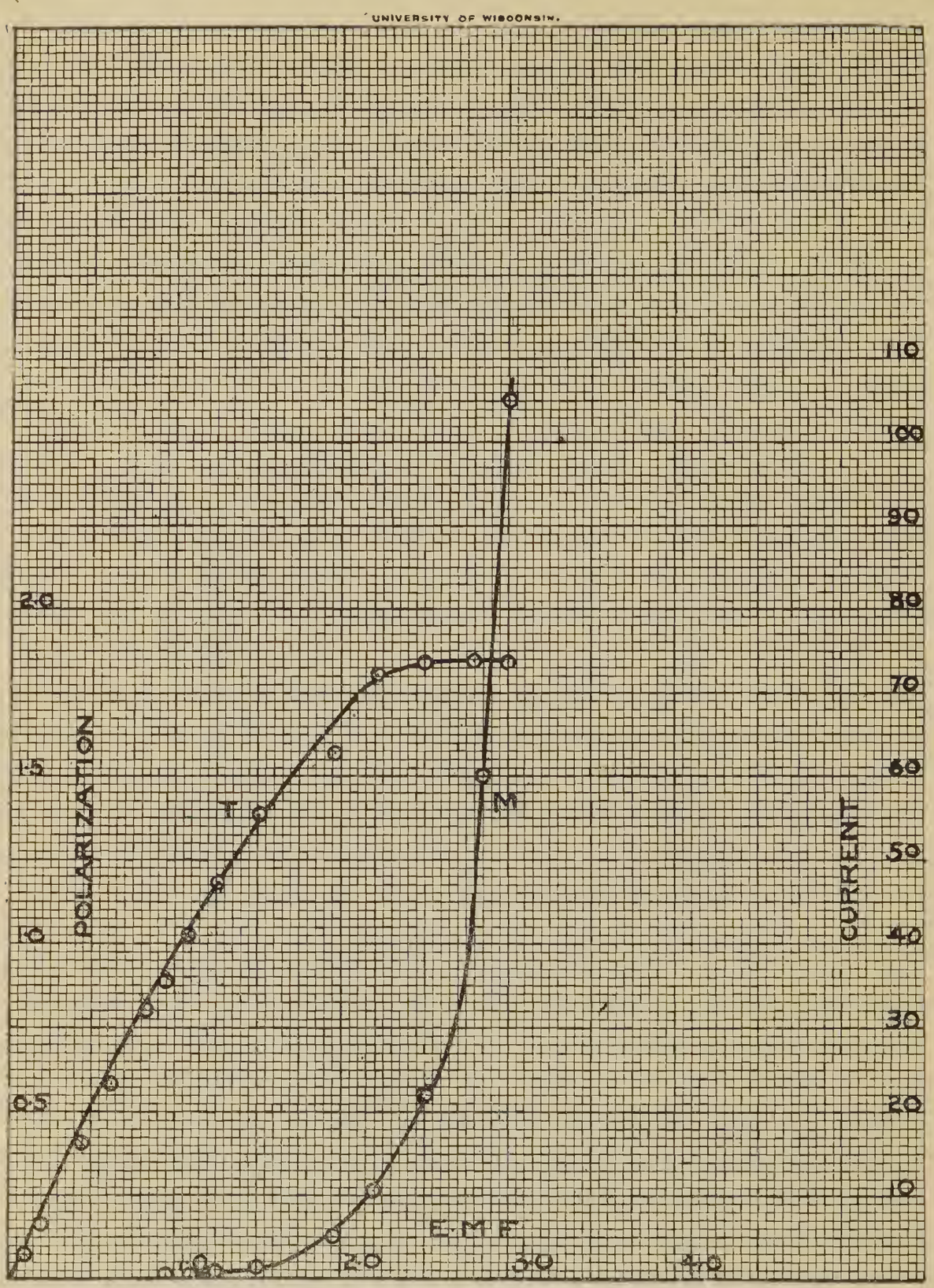


Fig. 2. Electrolysis of n.NaCl.—Carbon Electrodes.

The only possible part that the resistance of a gas film can play is to that small extent by which the polarization falls short of equaling the impressed E. M. F. The method of reading the polarization consisted in opening the line switch with one hand

and afterward closing the key of the galvanometer with the other, so that an appreciable interval elapsed between the breaking of the circuit and the reading of the galvanometer. It is therefore probable that the actual values of the polarization are slightly higher than the values recorded.

TABLE III.

Electrolyte, Normal $CuSO_4$. Electrodes, platinum.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization Volts
0.25	0	0.25
.50	0	.43
.75	0	.71
1.00	0	.90
1.25	0	1.13
1.50	1.	1.30
1.75	7.	1.36
2.0	11.	1.40
2.25	37.	1.40
2.50	53.5	1.40
2.75	70.	1.39
3.00	85.	1.41
3.25	102.	1.41
3.50	119.	1.43
3.75	136.	1.43

Table III and Fig. 3 show similar observations for normal copper sulphate with electrodes of sheet platinum one centimeter square. The general character of the curves is the same as for sodium chloride. It is to be noted that in this case gas is liberated only at the anode, and if it were the resistance of a gas film which prevents the passage of the current below 1.25 volts, this action would be confined to the anode, and the single gas film there would have to be quite as effective as the two films, one at each electrode, in the case of common salt.

The cause of the polarization is indicated by the behavior of the ammeter needle. When the E. M. F. is 0.5 volts, or any other value below the decomposition point, if the circuit be opened for a minute, and then closed again, at the instant of closing there is a considerable rush of current, which in a second or two dies away to zero, the value of the permanent current for the E. M. F. applied. When the circuit was open there was little or no polarization at the electrodes, and on closing the circuit a flow of

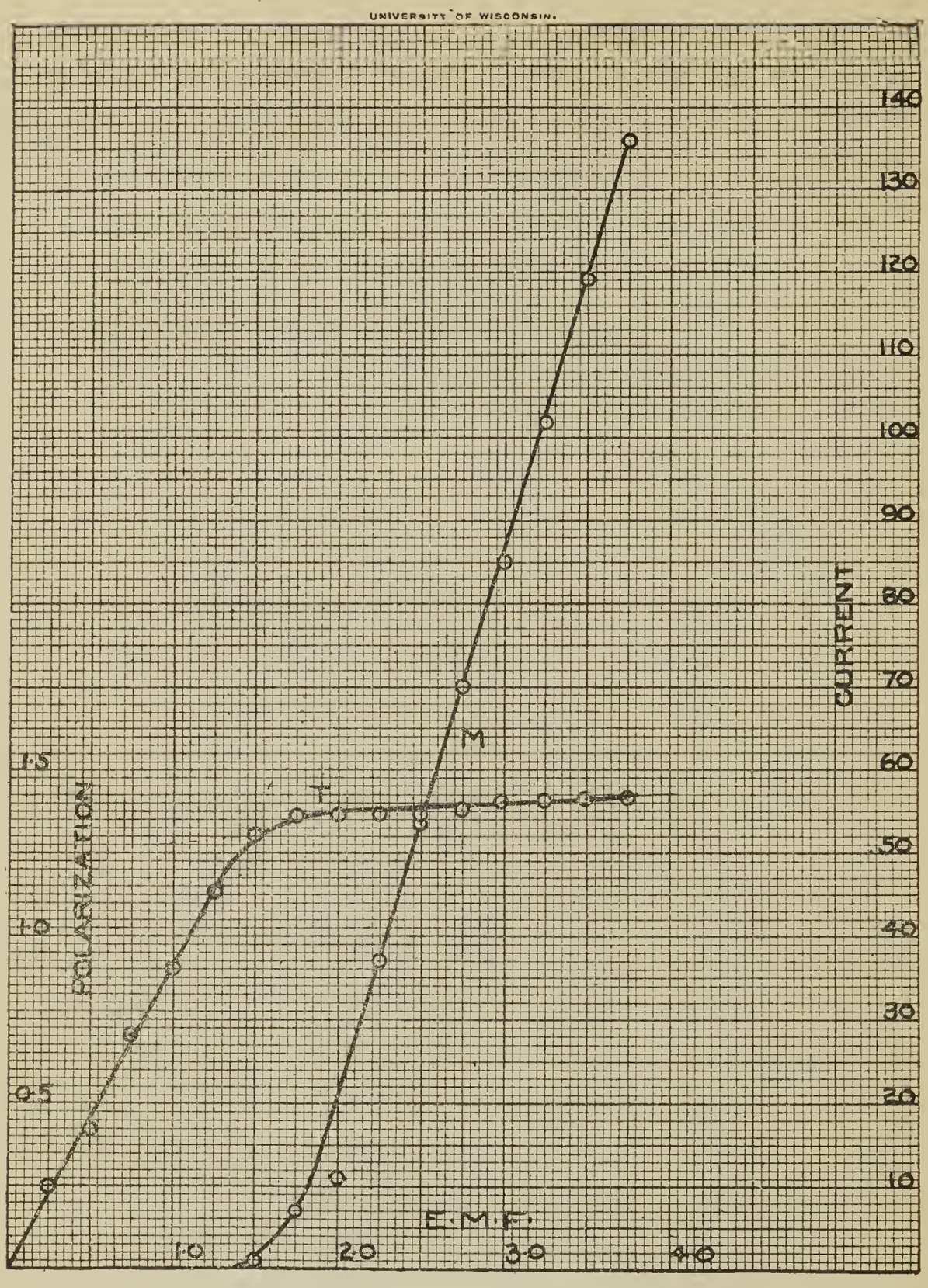


FIG. 3. Electrolysis of n.$CuSO_4$—Platinum Electrodes.

current began according to Ohm's law, just as it would flow through a wire, but, as a result of the deposition of the products of electrolysis at the electrodes, an increasing counter-electromotive force was produced, which finally attained the value of the impressed E. M. F. and stopped the flow of current.

The "residual current," that permanent current, normally so small as to escape notice, which flows through electrolytes at any constant E. M. F. below the decomposition pressure, is only the current required to deposit products of electrolysis equal in amount to those dissolved by the electrolyte or otherwise removed.

By the introduction of a third electrode and the measurement of the differences of potential between this and the anode and cathode, it is possible to ascertain what proportion of the total polarization is contributed by the anode and what by the cathode. The most satisfactory reference electrode to use for this purpose is the "normal calomel electrode," so well known that a description of it is unnecessary.

TABLE IV.

Electrolyte, normal $CuSO_4$. Electrodes, platinum.

Impressed E.M.F. Volts	Current Milli-amperes	Polarization Anode volts	Cathode volts	Total volts
0.05	0	—0.882	—0.839	0.031
.25	0	—.903	—.689	.236
.48	0	—1.118	—.646	.460
.72	0	—1.355	—.646	.709
.96	0	—1.591	—.642	.962
1.20	0	—1.763	—.581	1.185
1.44	0.5	—1.883	—.560	1.344
1.68	5.	—2.020	—.560	1.460
1.92	18.	—2.012	—.560	1.452
2.17	33.	—2.020	—.560	1.460
2.42	49.5	—2.020	—.560	1.460

Table IV and Fig. 4 show the results of repeating the electrolysis of normal copper sulphate and determining the polarization at each electrode. The current curve, M., and the curve of the total polarization, T, are as in the previous experiment. The curves of polarization of the anode, A, and of the cathode, C, are especially interesting. The initial readings of polarization at anode and cathode, before any external E. M. F. was applied to them, was omitted by the student who performed this experiment, but if curves A and C were extended backward to obtain the value of the polarization at zero E. M. F., both electrodes would show about 0.77 volts, the single potential of platinum in this electrolyte. As the E. M. F. impressed upon the electrodes is increased, the curves A and C separate, the potential of the cathode increasing to

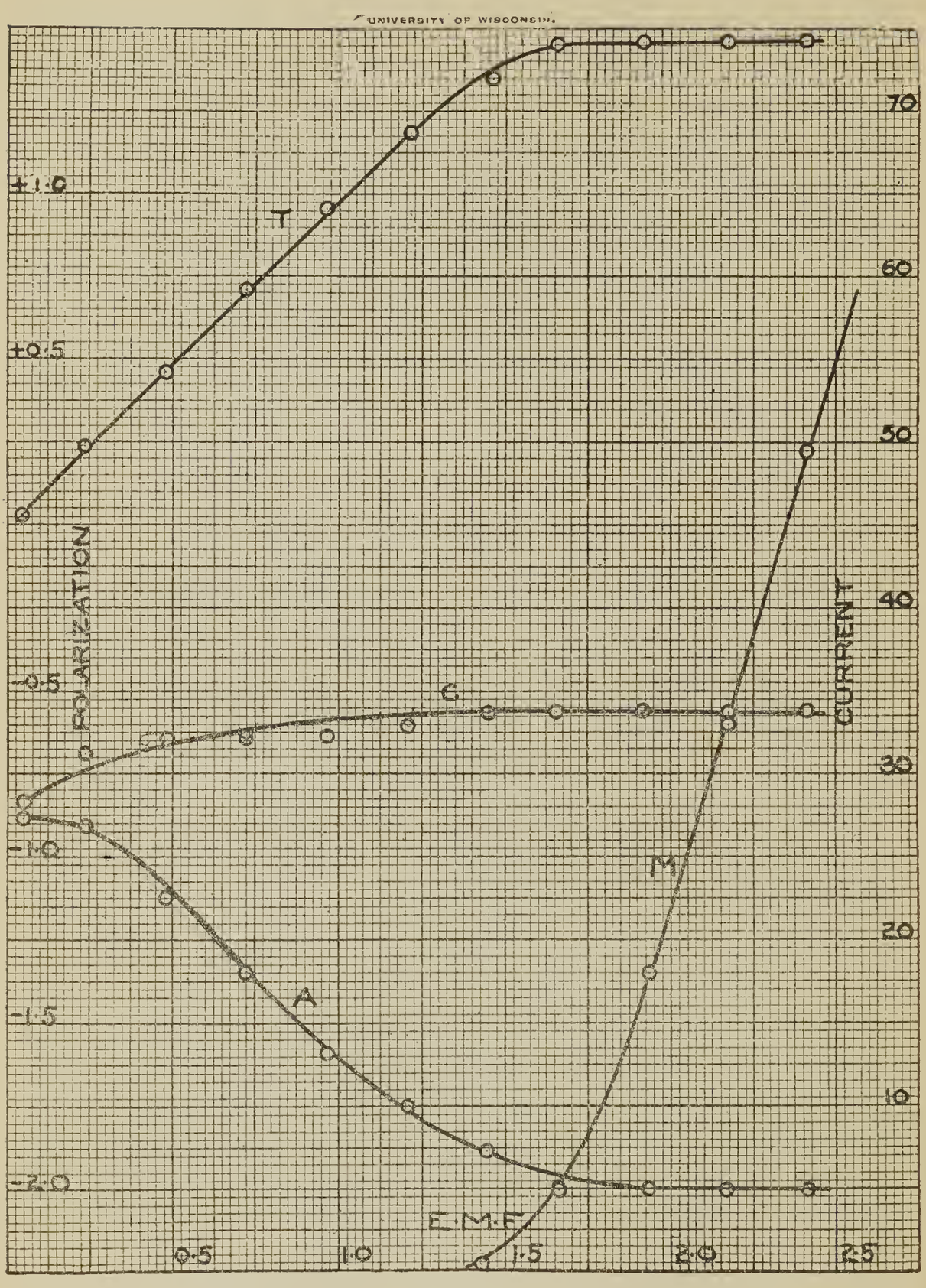


FIG. 4. Electrolysis of n.$CuSO_4$—Platinum Electrodes.

that of copper as its limit, and the potential of the anode diminishing to that of platinum saturated or coated with oxygen. It is seen that the polarization of the cathode quickly reaches a maximum, while that of the anode continues to increase until the impressed

E. M. F. reaches 1.75 volts. The cathode contributes only 22 percent to the total maximum polarization, the remainder being due to the anode. A comparison of the distances between curves A and C at various points, with values shown on curve T for the same E. M. F., shows how closely the separate potentials of anode and cathode agree with measurements of the total polarization.

TABLE V.

Electrolyte, zinc bromide. Electrodes, carbon.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization Anode Volts	Cathode Volts	Total Volts
0	0	—0.995	—0.992	0.009
0.05	0	—1.004	—.960	.037
.15	0	—1.050	—.951	.102
.25	0	—1.137	—.919	.215
.48	0.5	—1.245	—.809	.429
.72	0.7	—1.251	—.575	.667
.96	0.7	—1.253	—.342	.893
1.20	0.8	—1.271	—.148	1.122
1.44	2.5	—1.285	+.026	1.311
1.68	18.	—1.315	+.165	1.479
1.92	43.5	—1.323	+.368	1.654
2.17	119.	—1.362	+.456	1.816
2.42	209.	—1.372	+.461	1.833
2.65	310.	—1.372	+.472	1.845
2.88	405.	—1.372	+.484	1.856
3.13	500.	—1.372	+.484	1.856
3.38	600.	—1.372	+.484	1.856
3.62	695.	—1.401	+.461	1.862
3.86	795.	—1.401	+.461	1.862
4.11	925.	—1.401	+.461	1.862

Table V and Fig. 5 are the results of the electrolysis of a solution of zinc bromide with carbon electrodes. The cathode contributes 78 percent of the 1.86 volts total polarization, while the anode supplies the remaining 22 percent. The electrolysis of zinc bromide effectually disposes of any claim that the failure to obtain a visible current with the first application of E. M. F. to electrolytes is due to the resistance of a gas film at either electrode. No gas is evolved in this case, except that at a very high current density a little hydrogen may be deposited along with the zinc at the cathode.

The curves for the cathode in figures 5 and 6 show a gradual change from electrodes of platinum to copper and zinc, respectively. Similarly, the anode curves represent the change from a

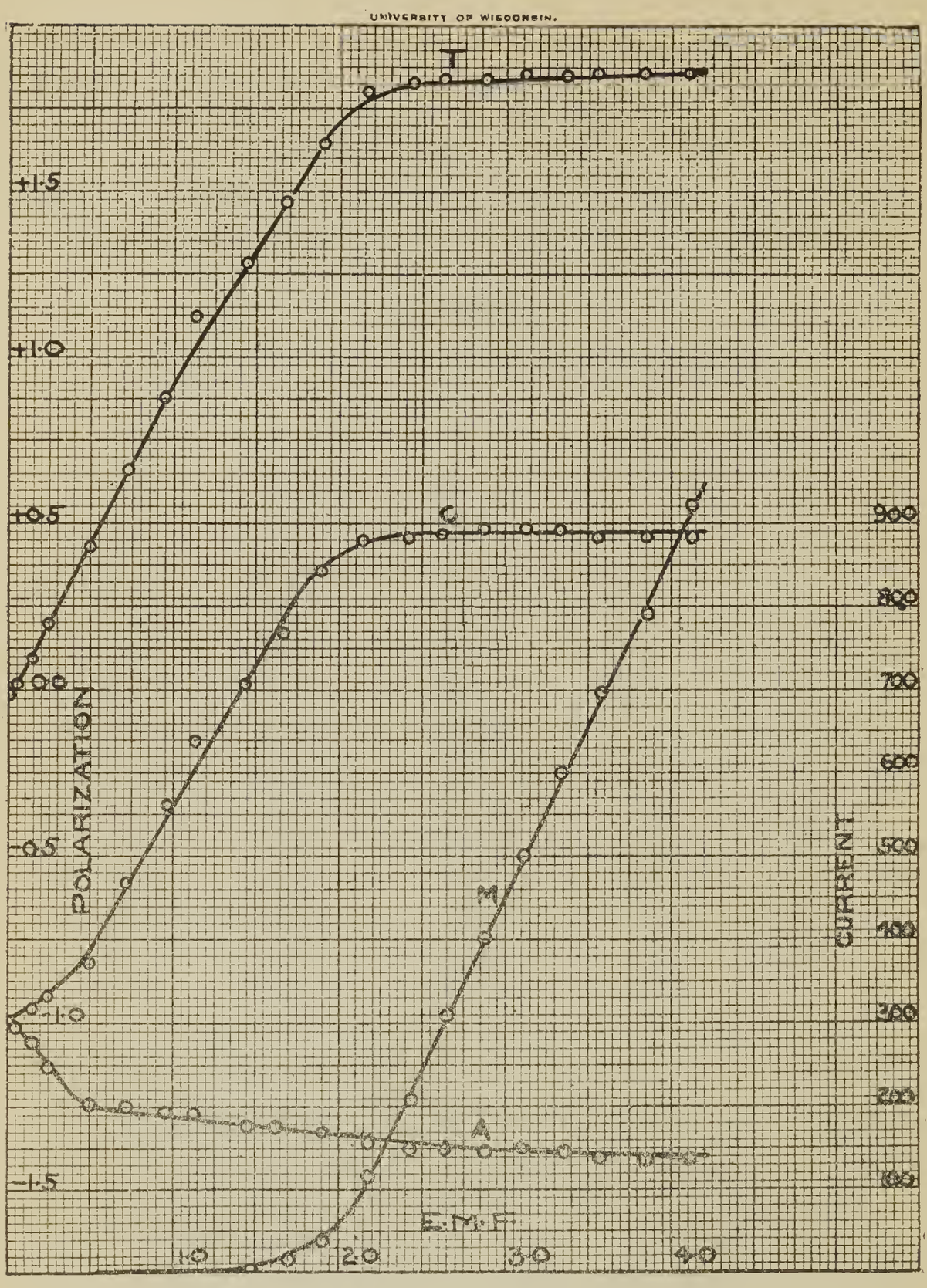


FIG. 5. Electrolysis of $ZnBr_2$—Carbon Electrodes.

platinum electrode making contact with the original solution, to platinum saturated or alloyed with oxygen and with bromine, respectively, making contact with an electrolyte saturated with these products of electrolysis. The source of the counter-electromotive force, then is of the same nature as the E. M. F. of any

primary, or storage cell, viz., it is the result of an unsymmetrical electrochemical system, consisting of two electrodes in one or more electrolytes. Before electrolysis the electrolytic cell was symmetrical consisting of like electrodes in an electrolyte of uniform composition, concentration and temperature, and therefore the E. M. F. of the cell was zero. With copper sulphate the application of an E. M. F. causes the system to become unsymmetrical, by the deposition of copper at the cathode and oxygen at the anode. The E. M. F. of this little copper-oxygen storage cell, which, as in all storage cells, is opposite in direction to the charging E. M. F., continues to increase in magnitude, as more and more copper and oxygen are deposited, until its E. M. F. equals the impressed E. M. F., when the flow of current ceases. All this may occupy one or two seconds. With each increase of impressed E. M. F. this process is repeated, until the value of the impressed E. M. F. exceeds that attainable by the little storage cell; then a permanent current flows.

Having considered several cases of electrolysis with insoluble electrodes, it will now be of interest to use a soluble anode.

TABLE VI.

Electrolyte, acid $CuSO_4$. Electrodes, copper.

Impressed E.M.F. Volts	Current Milli-amperes	Polarization Anode Volts	Cathode Volts	Total Volts
0	0	—0.553	—0.563	0.001
0.15	2.9	—.556	—.538	.017
.25	10.7	—.556	—.545	.015
.50	31.	—.560	—.545	.020
.70	50.	—.560	—.545	.017
1.00	82.	—.563	—.543	.022
1.25	105.	—.567	—.538	.025
1.50	130.	—.560	—.531	.030
1.75	152.	—.567	—.531	.032
2.25	182.	—.567	—.519	.045
2.75	232.	—.571	—.512	.060
3.25	295.	—.574	—.502	.076
3.75	350.	—.579	—.499	.087
4.75	325. (*a*)	—.574	—.487	.087
5.00	380.	—.574	—.487	.089

(*a*) The current varies between 250 and 400.

Table VI and Fig. 6 show the action of copper electrodes, 1 x 2 cm., with only one side exposed, in the acid copper sulphate solu-

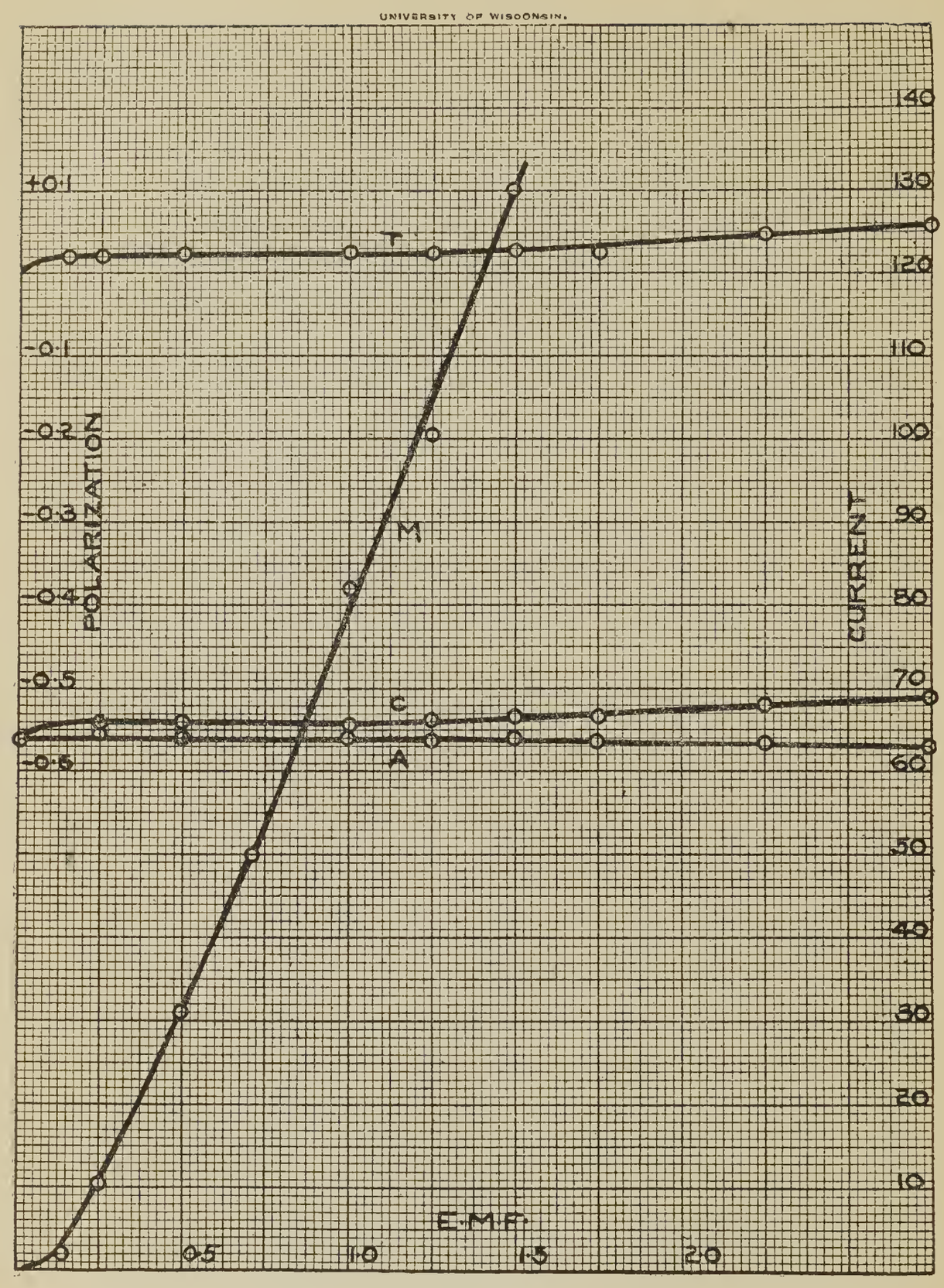


FIG. 6. Electrolysis of Acidified $CuSO_4$, Electrodes Copper, 1 x 2 cm., one side only exposed. Current Density: A. per Sq. foot = milliamperes used ÷ 2.

tion as used for electro-plating. The current-E. M. F. curve is almost like that for a metallic conductor. The reason for this is seen on examining the polarization curves. The greatest value for the total polarization was 0.06 volts instead of 1.46 obtained for

copper sulphate when platinum electrodes were used. It is this failure of the polarization to rise to any considerable value, which makes the current-E. M. F. curve so different from those of the other electrolytes. At the lowest E. M. F., 0.15 volt, the total polarization had already attained to 20 per cent. of its highest value. Eighty-five percent of the greatest total polarization is found at the cathode. It is to be noted that the polarization shows no evidence of having reached a maximum, as it did with the insoluble electrodes. It is evident that had a greater E. M. F. been applied, a still larger polarization would have resulted. It might well be asked how there can be any polarization when at the outset, and also at the end, the system consists of two copper electrodes in a solution of copper sulphate. If such an electrolytic cell as this is projected on a screen by means of a stereopticon, the reason for polarization appears. At the cathode there is formed, as a result of the deposition of copper, a layer of dilute solution in contact with the cathode. It is well known that the value of the potential set up by a metal making contact with a solution is affected by the concentration of the solution. Copper in copper sulphate is no exception to this rule. Diffusion and the circulation caused by differences in density tend to destroy this film of dilute electrolyte bathing the cathode, so that the degree of dilution attained may be expressed as a state of dynamic equilibrium here between the electric current which produces it and the above forces which would destroy it. It is evident that the higher the current density at the cathode, the more dilute will be the electrolyte which is in immediate contact with it. The anode, on the other hand, is surrounded by a layer of electrolyte which is more concentrated than the original solution; but as this dense electrolyte rapidly streams down and collects as a layer across the bottom of the cell, it might be expected that increase of current would have less effect upon anode polarization than upon that at the cathode, and this is shown to be the case.

The examples of electrolysis so far considered show that:

1. Polarization is responsible for the phenomenon of decomposition pressure in electrolytes.

2. The total polarization may be resolved into two components, the one at the anode, the other at the cathode.

3. Since it is polarization which prevents the flow of current in accordance with Ohm's law, the residual current is the equivalent in current of the rate of depolarization of the electrodes by the electrolyte.

Moreover, if electrolysis causes a change in the material of an electrode, or of the electrolyte in immediate contact with it, the polarization at the electrode is large. This is the case with an insoluble anode, and usually so for a cathode whose position in the electrochemical series is far from that of the element which is deposited upon it by the current.

If the chemical composition of the electrode and of the electrolyte in contact with it are not changed, the polarization will be small. This occurs with a soluble anode and with a cathode of the same material as that deposited by the current.

The data in the tables was, in the main, secured by students in the regular laboratory experiments in electrochemistry, and this paper is presented with the hope that it may prove useful to students who are engaged in similar work. For the plotting of the curves, the author is indebted to Mr. W. B. Schulte.

Laboratory of Applied Electrochemistry,
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DISCUSSION.

Prof. J. W. Richards: I think this is largely a very careful repetition of work which has already been done, and does not carry with it any disclosures or any new principles. I think, however, that the data and the curves given will furnish a good basis for careful discussions of the phenomena of back-electromotive force.

Mr. Carl Hering: It seems to me that Dr. Watts merely gives this phenomenon a name; giving a thing a name is not giving an explanation. It is a fundamental principle that a current multiplied by an electromotive force represents energy. If a current is passed against a counter-electromotive force, it must represent energy, and energy which is not in the form of

heat; in an electric motor it is in the form of motion; in a cell it is in the form of chemical energy. It seems to me the explanation of this counter-electromotive force, which the author calls polarization, is simply that some chemical energy is being stored up somewhere; electrical energy is being changed into chemical energy of some kind.

In connection with the latter part of the paper, where Dr. Watts compares the two electrodes with the calomel cell, I recall a method I used a good many years ago in testing accumulators. It consists in having in the cell two other plates, which are exactly like those that you are testing except that they are not in circuit and may be quite small. For instance, I used two small, fully charged accumulator plates, one positive and one negative, which I inserted in the accumulator and then measured the voltage between each of the test plates and the corresponding accumulator plate. In that way I obtained an indication of the condition of the large plates with reference to the normal test plates, which were not in circuit. The results were quite instructive.

In connection with this subject, although not bearing on it directly, I would like again to bring up the question of the origin of the energy of the expansion of the gases set free. When gas is liberated in electrolysis there is an expansion of, I think, about 1,600 times the volume; that is, the gases, oxygen and hydrogen, after they are set free, have a volume about 1,600 times that of the water from which they are formed. Hence there has been a very great expansion against atmospheric pressure, and that requires energy. The question is, where does that energy come from; does it come from the current or from the heat of the liquid? I think an investigation of this question might lead to some interesting results.

PROF. RICHARDS: In most of these tables there is given a statement of the first-applied electromotive force, showing no current in milli-amperes. My experience has been that with almost any applied electromotive force, under similar conditions, you can find a current if you have the ammeter delicate enough to measure it. The fact of "no current" means that the milli-ammeter was not delicate enough to measure the current. With a micro-ammeter Dr. Watts would have gotten readings all

the way down to the first-applied electromotive force which could have been put on the cell.

Dr. Watts (*Communicated*): This paper is an attempt to set forth the facts in regard to the relation between current and impressed electromotive force in several different electrolytic cells and to point out that, in those cases in which the flow of current is not in accordance with Ohm's law, there exists a counter-electromotive force which partially or completely, as the case may be, nullifies the impressed e. m. f. and so causes the phenomenon of the decomposition voltage.

While agreeing with Mr. Hering when he says that "giving a thing a name is not giving an explanation," the writer was under the impression that he had included the explanation as well as the name. On pages 94-98, 101, 103, 105 and 106 the cause of the counter-electromotive force is traced to the changes produced in the materials of the electrodes by the passage of current, and it is there stated that "the source of the counter-electromotive force is of the same nature as the e. m. f. of any primary or secondary cell." Since an explanation of any new or imperfectly understood phenomenon in nature consists in showing that it has a definite relation to other and well-known phenomena, it is hoped that the above may be accepted as an explanation of decomposition voltage.

A paper presented at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 7, 1911, President Wm. H. Walker in the Chair.

ELECTRIC DISCHARGES IN GASES AT REDUCED PRESSURE.

By Louis A. Parsons.

A study of the phenomena occurring during the passage of a current of electricity through a gas is of the greatest importance as regards the fundamental theories of electricity and matter. Though this is essentially a very modern field (the greater part of the work having been done in the last decade and almost all within the last two), it is a vast one and is most fascinating, though difficult. Of this field there are two general divisions: The electric conduction of gases at ordinary pressures (non-luminous), and the luminous discharges in gases in vacuum tubes at reduced pressures. It is in this latter field where the most beautiful and wonderful effects are observed, and this is the oldest field. Faraday observed and minutely described the phenomena of the luminous discharge in Geissler tubes as far back as 1832, and Plücker[1] in 1858 described most of the common phenomena and effects in such tubes which we know at the present day, and as regards the theory we are scarcely more than beginning to form definite ideas. The more we observe, the more wonderful it all appears, and often the more complicated. Someone is needed now to give us a simple, clear and comprehensive theory to cover the whole field, if such be not too much to expect.

Much, however, has been done in the way of showing us what goes on inside the vacuum tube. Of the names of the prominent investigators here, Plücker, Hittorf, Hertz, Warburg, Goldstein, Villard, etc., that of J. J. Thomson, of the Cavendish Laboratory, stands out the most prominently not only because of his own work and of those in his laboratory, but because of the splendid way in which he has presented as a connected whole

[1] Pogg. Annalen, **103**, 88 (1858).

the work of other investigators, in his "Conduction of Electricity Through Gases."[2]

Suppose we take a glass tube of considerable size, with two metallic electrodes sealed in it, arranged so that gas (hydrogen, say) may be admitted or pumped out at will, and send through it a steady direct current of high potential. As the pressure is gradually reduced, a point is reached where the current will suddenly start through the tube, this occurring at a higher pressure the greater the potential difference between the electrodes and (through ordinary ranges) the closer the electrodes are together. The potential necessary to produce a discharge also depends upon the shape of the electrodes and upon the nature of the gas. In air at atmospheric pressure a potential difference of about 30,000 volts is necessary to cause a discharge across a gap 1 cm. wide. As the pressure is decreased, the potential necessary to produce a spark decreases almost linearly until a certain critical pressure is reached, of the order of a millimeter of mercury column, giving the minimum potential, after which it very rapidly rises as the pressure is further decreased. The minimum potential has been found to be constant for a given gas, being independent of the distance between the electrodes. For air, its value is about 351 volts; for hydrogen, 280 volts and for carbon dioxide, 420 volts. The critical pressure is higher the closer the electrodes are together, the product of the critical pressure and the electrode distance being constant, equal to about 12 for hydrogen and 5 for carbon dioxide (both being expressed in millimeters). Paschen has shown that for the whole range of pressures the potential difference necessary to start the discharge depends only on the product of the pressure and the distance between the electrodes; hence a set of observations of the variation of potential with pressure for a fixed electrode distance enables us to determine the potential for any pressure and any distance.

If the distance between electrodes is small enough for a spark to start at high pressures, a noisy luminous spark may be maintained between electrodes, certainly will be if an induction coil is used, or sufficient capacity in parallel with the electrode gas when a battery or dynamo is used. The spark discharge in

[2] Cambridge University Press.

such a case is always oscillatory, as may be shown by a revolving mirror. Such a discharge in hydrogen produces a thick red spark giving the four-line spectrum very bright. If this discharge is made non-oscillatory, it passes over into the arc form with bright spots or patches on the electrodes and a pale aureole or flame-like discharge between them. At lower pressures, say about 1/10 of an atmosphere, the discharge with a steady current due to an e. m. f., say, of a few thousand volts, consists of a bright spot on the anode and a velvety cap on the cathode, while the space between is entirely dark. With decreasing pressure, the cap covers gradually the entire cathode and swells up, a dark layer appearing in it, which itself expands as the pressure decreases; at the same time the glow increases on the anode and

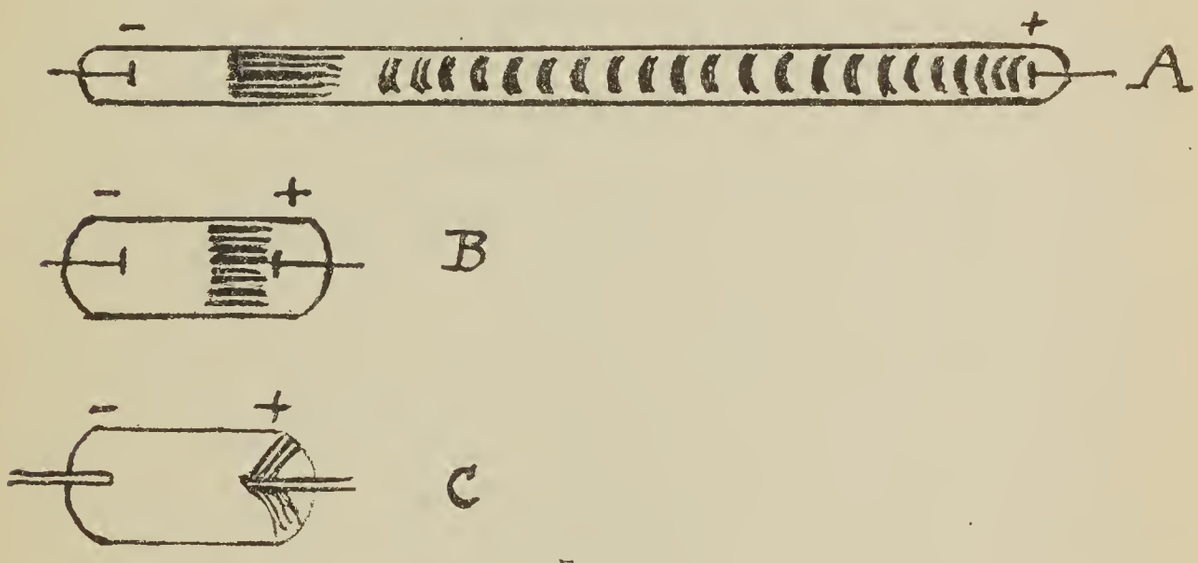


FIG. 1.

reaches out toward the cathode. At pressures of a few millimeters the phenomena are clearly defined. The surface of the cathode is covered with a bright glow; outside of this is a dark space, extending normally in all directions to equal distances, having the form of the surface of the cathode. This is known as the "Crookes Dark Space." Outside is a bright glow, the negative glow, diffusing gradually outward. The anode may be covered with a glow or only its tip may be bright, and extending outwards from it toward the cathode is a bright glow known as the positive column, which in some cases is unbroken, resembling a long brush, and in others is broken up into many button-like sections, concave toward the anode, known as striations. Between the positive column and the cathode glow there is

another dark space, not always well defined, known as the "Faraday Dark Space." The length of the Crookes dark space depends principally upon the pressure in the tube, though it also depends upon the current, increasing slightly as the current increases, and upon the diameter of the tube (unless the tube is quite large), but seems to be independent of the distance between the electrodes. The length increases with decreasing pressure, and is either equal to or in a simple way dependent upon the mean free path of a molecule, or a corpuscle, of the gas, and Thomson has shown that the two are of the same order of magnitude. The extent of the negative glow also increases with decreasing pressure and does not seem to depend much on the size of the tube. The positive column, on the other hand, seems to be determined by the shape and size of the tube. Elbert[3] gives 1.2 mm. as the length of the dark space at a pressure of 2 mm. in air, and 7 mm. at a pressure of 0.19 mm. In hydrogen the length is 7 mm. at a pressure of 0.4 mm.; at a pressure of 0.72 mm. the length of the dark space in hydrogen is 5 mm., and in oxygen, 2 mm. At pressures as low as 0.01 mm. the length of the dark space may be more than 10 cm.

Suppose we have a tube 1 meter long. The dark space may then extend 10 cm., the negative glow an equal amount beyond, and the positive column the rest of the distance. If the distance between the electrodes should be less than 10 cm., the positive column will be absent and the cathode dark space contracted somewhat between the electrodes, as in (B). If the distance between the electrodes is, say, 5 cm., a discharge may be blown back from the tip of the anode, as in (C). In this case the potential difference between the electrodes is quite high, and if the distance between them is too small, or the tube too small, the discharge cannot pass at all.

The total number of striations in the positive column depends only on the length of the tube, and may reach several hundred. The distance between the striations depends upon the diameter of the tube, the pressure of the gas and the current in the tube, being greater the larger the diameter (until a considerable diameter is reached), the lower the pressure and the greater the current.

[3] Conduction of Electricity through Gases, 2d Edition, pp. 542-6.

The rate of fall of potential in passing from the anode to the cathode along the path of discharge is not constant, *i. e.*, the electric force is not uniform. Experiments show that by far the greater part of the total fall of potential occurs in the vicinity of the cathode, in the Crookes dark space, and hence the electric force is very great here. Recent experiments by Aston[4] at the Cavendish Laboratory show that the electric force is greatest very close to the cathode, and decreases uniformly to the outer edge of the dark space, where it becomes practically zero and remains so throughout the negative glow, and also in the Faraday dark space. In the positive column, if unstriated, the force, or the rise of potential as we approach the anode, is constant. Some observers have found a sudden drop of potential very near the anode. If the positive column is striated, the force is a maximum in the striations and practically zero in the dark spaces. The negative side of each striation acts as a cathode, and the positive side as an anode. The fall of potential in the Crookes dark space is called the "cathode fall of potential." This is independent of the current in the tube (and consequently of the e. m. f.) until the cathode glow covers the entire cathode; for greater current it increases with increasing current. This cathode fall of potential depends upon the nature of the gas, and is greatly affected by small traces of an impurity, especially oxygen, and depends on the nature of the electrode, though for most dense metals it is practically the same. In pure nitrogen, Warburg[5] found the cathode fall to be 230 volts with platinum electrodes and 207 with aluminium electrodes, while the total minimum discharge potential is 251 volts. In hydrogen the cathode fall is about 300 volts, and the minimum discharge potential between 302 and 308. Evidently any means of eliminating or greatly reducing the cathode fall of potential would result in a vastly increased current in the tube (an increased luminosity which is of great importance in spectroscopic work) for a given voltage and enable one to use comparatively low voltages. Hittorf found that the cathode fall was greatly reduced when the cathode was heated to redness. Wehnelt found that it was greatly reduced and the currents vastly increased by coating the cathode with lime, which

[4] Proc. Royal Society, 84a, 536 (1910).

[5] Conduction of Electricity through Gases, 2d Edition, p. 537.

was by some means heated to redness. Such a Wehnelt cathode enables us to get a current of the order of magnitude of an ampere with an ordinary 110-volt direct current supply, whereas the usual current in a vacuum tube is expressed in milliamperes with an induction coil giving, say, 100,000 volts.

If in a tube with electrodes a considerable distance apart the pressure is reduced until the dark space is as large as the tube, the visible discharge ceases. But now invisible rays come out from the cathode in straight lines, producing a yellowish-green phosphorescence where they strike the glass and heating objects placed in their path. These rays were first observed by Plücker in 1859 and by his pupil, Hittorf, who showed that shadows were cast on the glass by objects in their path, and were called by Goldstein, cathode rays. They produce chemical changes and phosphorescence in objects struck, and give rise to the X-rays. They have been thoroughly studied by a large number of investigators, notably Villard, Goldstein and J. J. Thomson, and these investigations have led to the belief that all vacuum tube phenomena can be explained on the theory of moving ions or charged particles in the gas. Goldstein had advanced the theory that the rays were ether waves similar to light, and this view was at first generally accepted in Germany, but Crookes believed that they consisted of electrified particles shot out at right angles from the surface of the cathode, and this theory is now universally accepted.

Though the cathode rays themselves are ordinarily invisible, they may be shown either by using a phosphorescent screen in the tube, or by arranging to produce the cathode discharge in pure oxygen, in which the path is visible. By allowing the rays to pass through a small opening in a plate in the tube, a narrow pencil is obtained extending straight out from the cathode surface, which can be deflected by an electrostatic field or by a magnet, the deflection being such as would be produced by a stream of negatively charged particles, and by allowing the stream to pass through a cylinder connected to an electrometer they have been found to be negatively charged. Assuming the ordinary laws of electric and magnetic forces, J. J. Thomson calculated the velocity of these assumed negative particles and of e/m the ratio of the charge to the mass of the "corpuscle."

These results have been checked by many later observations by different men. The velocity is of the order of the velocity of light, and the value of e/m for the latest experiments $= 1.76 \times 10^7$ e. s. units. The value of e was found in case of ions produced by X-rays by the formation of a cloud by the condensation of a vapor on these corpuscles or ions. The total number of ions was found by weighing the amount of water in the cloud, and their size determined from the rate of fall of the cloud, and, knowing the total current passing through the gas and the velocity of the ions, the charge on one corpuscle was calculated. This was found to be the same as the charge carried on an ion in electrolysis (7×10^{-10} e. s. units). More recently the value of e has been obtained by different observers, notably Professor Millikan,[6] of Chicago, by condensing some vapor (as oil) on the corpuscles and actually observing their motion with a microscope. These results give for the mass of the corpuscle about 1/1000 the mass of an hydrogen atom.

By using a cathode pierced by holes, Goldstein[7] discovered streams of positively charged particles or ions going back from the cathode, which have been called canal rays, or positive rays. There are a number of different kinds of positive rays that have been observed by J. J. Thomson[8] and others in cathode ray tubes. One kind, known as retrograde rays, apparently originates near the cathode and moves away from the cathode in the same direction as a cathode ray. Canal rays have recently, by Goldstein[9] (and others), been observed with a simple wire cathode without any "canals," and Goldstein now believes that these "canal" rays are produced in the luminous cathode layer itself. As a result of his latest experiments, J. J. Thomson[8] enumerates three cases of positive rays: (1) Undeflected rays, not affected by electric and magnetic forces, due probably to recombinations of positive and negative ions; (2) secondary rays produced by (1) and due to dissociation of the former or of molecules of the gas, whose velocity is independent of the nature of the gas and of the p. d. between the electrodes; and (3) positive rays characteristic of the gas and dependent upon the p. d.

[6] Trans. Amer. Electrochem. Soc. **18**, 283 (1910).
[7] Wied. Annal. **44**, 45 (1898).
[8] Phil. Mag. pp. 752-767 (1910).
[9] Phys. Zeit. **11**, 873-880 (1910).

In the discharge tube at any pressure we are concerned with these ions of the gas. The negative ions may consist of separate electrons (or corpuscles), as in the cathode rays, or of electrons attached to atoms or molecules or aggregates of molecules. The positive rays may be due to atoms with a deficiency of electrons (according to one theory) or combinations of such atoms. On this view there is but one kind of electricity and one ultimate atom of electricity, the negative electron. But J. Becquerel,[10] about two years ago, concluded from his experiments that there is a positive electron of the same size, and J. J. Thomson[11] has recently advanced the view of a positive unit of electricity of the same order of magnitude as the hydrogen atom.

An interesting question in regard to the electric discharge in vacuum tubes is as to what is the cause of the light emitted. Is the radiation of light produced by accelerations of the electrons (or atoms) at a time of dissociation, or of recombination of ions, and does it last only so long as this dissociation (or recombination) is taking place, or persist for a certain length of time after that? It may be that the same gas may give different spectra when excited by an electric charge according as the light emission is due to combination of ions, or dissociation, or to the vibrations of positive and negative electrons more or less connected. Our present knowledge of the whole subject does not enable us to definitely answer these questions.

Villard[12] has shown that when cathode rays move at right angles to magnetic fields, they are bent into circles around the lines of force if the field is uniform; if the rays form a small angle to this direction, their path is a spiral (helix) with axis along the magnetic lines. If the velocity is not uniform, the separate convolutions are successively further separated. If the magnetic field is not uniform, but decreases uniformly from a central axis, as in the case of a magnetic field between pole pieces of an ordinary magnet, the path of the rays (nearly perpendicular to the lines of force) consists of a sort of double spiral, the axis of the smaller convolution itself being a spiral; and he has beautiful photographs showing each of these effects.

Other very peculiar effects are produced by the magnetic field

[10] Comptes Rendus **146**, 1308-1314 (1908) and Electrician (London) **61**, 525 (1908).
[11] Phil. Mag. **18**, 821-845 (1909).
[12] Le Kadium **3**, 97 (1906).

on the visible discharge at higher pressures as well as on the cathode ray discharge. If we start with a magnetic field parallel to the axis of the electrodes and increase the strength of the field, the potential difference between the electrodes is decreased and varies greatly at a certain critical value of the field. At the same time, lines of discharge from the cathode follow the magnetic lines of force extending toward the anode, and often a peculiar discharge extends out from the anode toward the cathode. This increase in the current through the tube (or decrease of potential between the electrodes) also occurs with a discharge at right angles to the electrodes, under certain conditions. According to one explanation, the rays which in this case follow the lines of magnetic force are the same as the ordinary rays from the cathode, but Villard and others, notably Guoy[13] and Righi,[14] believe that we have here a new kind of rays which Villard calls "magneto-cathodic" rays, and Righi, "magnetic" rays. Righi claims that they consist of positive and negative ions which in their motion have come close to each other and, because of their mutual attractions, revolve about a common centre; he calls them "neutral doublets." It is not by any means certain, however, that any such "magnetic" rays, thus distinct in their nature from other positive and negative rays, exist in the vacuum tube discharge either at cathode-ray pressures or under the conditions of a luminous discharge. The subject needs certainly more study and investigation.

Physical Laboratory,
Johns Hopkins University,
March 25, 1911.

DISCUSSION.

Dr. W. R. Whitney: This paper, and that of Prof. Richardson, illustrate to my mind one of the objects to be gained by this organization, in that it gives material, very suitable material, for research in institutions of learning, where the men can follow,

[13] Comptes Rendus. **148**, 455-458 (1909).
[14] Journ. de Phys. **7**, 589-617 (1908).

and should follow, lines of pure research to ends which will ultimately benefit all of us. To make this clearer: it is practically impossible today, in commercial research, to investigate to any great extent the phenomena of ions, electrons, and corpuscles, and yet there is hardly any doubt that they form the fundamental basis of our entire electrical science, and we want just that sort of investigation. We want the professors to attend these meetings, and those having students working under them to realize that determining for example whether aluminum dissolves in cryolite as a metal or not, is a work of real importance.

I have been a professor in a school, and I know how hard it is to select what are believed to be suitable research problems. The average student in America is justified in our times in wishing to touch a little bit on the practical; if you give him something purely theoretical, I believe he is justified in looking askance at it, but if you show him that, although his work may not influence the world as he would like to influence it today, it may contribute largely to influence the work done fifty years from now, you can interest him.

President Wm. H. Walker: There is another phase to this general problem as far as the student and his interest is concerned, and that is the possibility of strictly scientific investigation being carried on in such a way as to give it a practical bearing; that is, because a problem has somewhere a touch of utility to it, that is no reason why it should not be just as valuable to work on as a scientific problem with no evident industrial application.

A paper read at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 7, 1911, President Wm. H. Walker in the Chair.

THE MECHANISM OF ELECTROLYTIC TRANSFER.

By Joseph W. Richards.

The writer has been an interested student of all the theories put forth to account for the continuous appearance of the products of decomposition of an electrolyte at the two electrodes, that is, in effect, for the transfer of each ion the average distance from the center of the electrolyte to the electrodes.

My attention has been profoundly attracted by a phenomenon which is of frequent occurrence, particularly in fused salts, viz., the deviation of a chemical compound from the simple or fixed atomic proportions. So frequent is this deviation in fused salts, and so important is it in a proper consideration of electrolysis, that it surprises me that it has been so little considered.

To illustrate and explain this phenomenon: If I melt iron pyrites, FeS_2, sulphur leaves it, and at a low temperature one has Fe_3S_4, Fe_5S_6, Fe_7S_8, or various approximations to FeS. By increase of temperature one passes by insensible gradations all the way to Fe_2S, and at electric furnace temperatures perhaps beyond this. Regard FeS a moment; when melted it can combine with sulphur and become $FeS+S_x$, or it can dissolve iron and become $FeS+Fe_y$.

Consider copper matte. Almost any matte can dissolve copper or iron and become more basic, or combine with more sulphur and become more acid. A chemical compound in absolutely atomic weight proportions is practically unknown in this whole class of compounds, when melted.

Silicates furnish another instance of indefinite or indeterminate chemical compounds. They appear to be largely mutual solutions of the constituent oxides in each other, in any proportions in which they happen to exist together.

In general, a rather extensive study of fused salts and compounds leads one to regard fixed atomic weight proportions as the

exception rather than the rule, in practical work. True, the definite normal compounds do exist in nature, in the solid state, let us say; but as soon as such are fused, or perhaps even when they go into solution in a solvent, they became susceptible to these abnormalities in composition, to these departures from the simple atomic proportions. This may be a necessary preliminary to the possibility of electrolysis.

Assume a tube full of melted PbS a meter long, with two unattackable electrodes. Pass an electric current, tending to separate out Pb at the cathode and S at the anode. The electrolyte is absolutely normal PbS, let us say, or $Pb_{1000}S_{1000}$ or any other multiple of PbS, before electrolysis begins. The instant current passes, PbS at both anode and cathode is distorted chemically out of the normal proportions. The removal of some small amount of the lead around the cathode leaves the PbS there slightly deficient in Pb. We might call it, for instance, $Pb_{999}S_{1000}$. The removal of some small amount of sulphur at the anode leaves the PbS there slightly deficient in S; we might say we have converted it into $Pb_{1000}S_{999}$.

Now, it is undoubtedly the fact that such compounds slightly removed from the normal composition of PbS are highly soluble and rapidly diffusible in melted PbS. It results that the deficit of lead at the cathode is quickly distributed throughout the whole electrolyte while the deficit of sulphur at the anode is similarly rapidly distributed throughout the electrolyte. This distribution of the two deficits at the two electrodes is by the known solubility of such intermediate products in the normal salt, and amounts to a virtual transfer of the two constituents *from the whole mass* of the electrolyte to the two electrodes.

According to this view, the transfer in electrolysis is essentially solubility and diffusion of these slightly abnormal compounds formed by electrochemical action at the two electrodes. It is essentially mutual solubility; it is occasioned by the electrolytic action at the two plates, but it is a physico-chemical effect, and is in no sense essentially electrical in its mechanism.

In short, the current passes through the electrolyte as through any other conductor, it simply passes; *how* we are still discussing, but most certainly by the same means in a liquid electrolyte as in a liquid metal. This is merely conduction.

The current produces chemical changes at the surface of the electrodes; it tends to take base out of the salt at the cathode and acid at the anode. It thus distorts to a very trifling amount, in any given instant, the chemical proportions of the compound in the immediate neighborhood of the electrodes. This is electrolysis, pure and simple.

These slight changes in chemical composition tend to equalize themselves throughout the body of the electrolyte, by mixture and diffusion, or mutual solubility. This virtually results in the electrolytic transfer; but my thesis is that the transfer occurs as the *result* of the electrolysis and is not the pre-existing mechanism of electrolysis.

DISCUSSION.

PROF. L. A. PARSONS: I notice Dr. Richards begins at the opposite end to where I began a while ago, but he did not venture to give the theory as to how the conduction occurs in the case of an ordinary copper wire, for instance; but says that the conduction in the case of the fused electrolyte probably occurs in the same way as in the metallic conductor; that the current produces electrolysis at the electrodes and that the electrolytic transfer is the result of that. I began at the opposite end, and was more interested in investigating the gases first, because they are simpler. In gaseous conduction there is a motion of electrons, and certain experiments, I believe, have established beyond any doubt the existence of these electrons; and their motion has been studied, in cases where they occur singly (not as aggregates). The ions, I would say, consist of atoms with an excess of electrons (negative ions) or deficient in electrons (positive ions), or electrons attached to groups of atoms, aggregates of molecules, in some cases very large.

The electron is the ultimate unit of negative electricity. So far the existence of a positive electron has not been proved, or, at least, is not generally accepted, though some experiments would seem to indicate it.

When we pass from the conduction in gases to conduction in

electrolytes, we have something, I believe, which is even a little more difficult to understand than the case of the gases, because the very fact that the gases seem so much more complicated is because we are there able to see a little further into the thing.

According to the theory of electrons, conduction in metals consists in the handing over of electrons from one molecule or atom to another, and may it not be, in the case of conduction in fused electrolytes, that in this transference of electrons or atoms or groups of atoms or molecules, you may in some cases have more electrons than in others, and that consequently they exert different forces of attraction upon the other atoms or combinations, and thus possibly cause different chemical combinations; so that we may have here, as suggested by Prof. Richards, chemical compounds which are not entirely rigid in their composition?

Mr. A. H. Cowles: I think the beginning of this study was with Faraday, when he developed the law that every chemical equivalent of monad elements carries in electrolysis a uniform equivalent of electricity, and every dyad element two such electrical equivalents, etc. When we have elements that are capable of more than one equivalence, or valency, and you fuse and electrolyze the compounds of such, you may form in the bath sub-salts in mixture with normal salts. This is due to the action of the bath on the metal deposited, through local action. After they are fused and at a high temperature, it is easy for the lower salts to pass to higher, especially in the case of oxygen salts, and therefore they appear to give you less than the electrochemical equivalent of deposit of metal on the cathodes than that which one would look for from Faraday's law. But still it does not alter the truth of the law. The oxidizing influence of the air and the formation of salts from the metal deposited have lessened the actual output.

When you fuse and form such electrolytic baths and fail to provide against the oxidizing influence of the atmosphere, you may obtain a low efficiency. Take, for instance, the electrolysis of sodium hydrate; there are two or three oxides of sodium, and if an oxide lower than the normal one be formed, it can be oxidized at the surface of the bath, thus consuming current through

repeated formation and decomposition. Again, if the metal sodium floats on the bath, it may be oxidized at the surface or be converted into chloride or fluoride, according to the materials employed, thus making the efficiency low and the process appear to disregard Faraday's law. Again, if you have an electrolytic bath under high temperature and under conditions where the walls of the vessel are conductive and in contact with the metal that is being deposited, and also in contact with the liquid of the bath, then you have the simple proposition of two short-circuited electrodes with a fluid between them capable of corroding one of the electrodes (the deposited metal) with the liberation of another product on the other electrode (the wall of the vessel, or the cathode material uncovered by deposit). This form of local action will lower the apparent efficiency of the process. While we have these various ways to account for the low apparent efficiency in many cases of electrolysis of fused salts, it is my impression that one will have to prove definitely that these phenomena are eliminated, before one can disprove Faraday's law.

Mr. A. H. Cowles (*Communicated*): It is the writer's experience that the metal aluminum as such cannot dissolve in a double-fluoride fused bath without local action and against the influence of a current that is depositing the same. With no current flowing, it will dissolve, forming a fluoride with an equivalent liberation of sodium. The higher the percentage of sodium fluoride in the bath, the more rapidly this takes place. If the percentage of aluminum fluoride be high in the bath, the temperature being about 900° C., the affinities become reversed and the metal sodium will pass into the bath and aluminum fluoride will become reduced, liberating aluminum; but in both of these instances local galvanic action undoubtedly plays its part, as is the case when one attempts to dissolve pure zinc in sulphuric acid and finds that it fails to dissolve freely until brought in contact with some more electro-negative element, whereupon it dissolves with great rapidity.

Prof. A. W. Smith (*Communicated*): I fail to find in Professor Richards' explanation of the mechanism of electrolysis any single adequate reason for him to thus so ruthlessly destroy, at one blow, the law of multiple proportion, upon which the

science of chemistry has erected such an elaborate structure, and the beautiful theory of Hittorf, the ionic transfer of which explains so satisfactorily, as far as I am aware, all of the known facts of electrolysis, both in aqueous and in fused solutions.

Simply because two substances are mutually soluble each in the other is no good reason to conclude that their component atoms are not combined in atomic ratio. The existence of a solution of hydrogen peroxide in water is not a good reason for saying that the atoms of hydrogen and oxygen are disregarding the law of definite proportion, and no more does it follow, because cuprous and cupric sulphide happen to dissolve each other mutually in mattes, that sulphur and copper are not combined in the manner they have for many years been credited with doing. The new explanation of electrolysis is still not clear to me, while the ionic theory seems adequate.

Prof. J. W. Richards (*Communicated*): Professor Parsons' remark that I began "at the opposite end" designates very well my fundamental idea. The ordinary explanation of electrolytic transfer begins with the assumption of a pre-existing electrolytic dissociation in the electrolyte, with pre-existing charged ions waiting for the application of an electric stress to start them towards the electrodes, and their migration towards the electrodes constitutes the mechanism of electrolytic transfer. I start "at the opposite end." I postulate simply the passage of the current through the electrolyte as through any other conductor, then the true electrochemical action taking place primarily at the surface of the electrodes, and then a virtual transfer of the parts of the electrolyte by a physico-chemical equalization throughout the electrolyte of the chemical inequalities produced at the electrodes by the electrochemical action. The electrolytic transfer is thus a *result* of the electrochemical action at the electrodes, and not the pre-existing cause of the electrochemical action.

Professor A. W. Smith's kindly remarks are very natural, but they rest on a slight misconception. Perhaps I did not state it clearly enough in my paper, but my conception of a fused electrolyte is that, for all practical purposes, and especially for considering the phenomena of electrolytic transfer, the fused material contains its constituents in indefinite as opposed to atomic, or simple multiple, proportions. When such melted

masses solidify, and especially when they crystallize, we get from them definite chemical compounds, such as chemistry describes by the hundreds, but are not these simply resulting from the differentiation of the melted material, and are we justified in postulating their actual existence in the melted mass? I think not; it seems to me that we must consider the melted mass *as a whole or unit*. Are not aqueous solutions compounds of the solute with indefinite amounts of the solvent? Is not carbon dissolved in melted iron simply dissolved carbon, although it does separate out on solidification as Fe_3C? In other words, combinations in *definite proportions* are the result of differentiation under *definite conditions*. I do not want for an instant to deny the existence of the law of simple and multiple proportions, but it does seem to me that we should recognize the conditions under which it operates or comes into play, and also those in which it is, for practical purposes, inoperative. The latter case is probably that of fused salts, and the recognition of this gives us another possible theory of electrolysis and electrolytic transfer.

Mr. Cowles speaks of fused salts in the ordinary aspect of mixtures of higher and lower salts in indefinite proportions. Thus he speaks of two or three oxides of sodium which might be present in a fused sodium hydrate bath. It is true, moreover, that we know those oxides separately, in the solid state. But, in a fused mixture, to all intents and purposes, the melt contains sodium and oxygen in indefinite proportions, and its percentage composition in sodium and oxygen is indefinite. This makes possible the explanation of electrolytic transfer given in my paper.

I doubt the accuracy of Mr. Cowles' statement that, with no current flowing, aluminum dissolves in a double-fluoride fused bath with liberation of an equivalent amount of sodium. That is contrary to my observation and experience.

In conclusion, I would say that I do not presume to have offered an unobjectionable theory for the phenomena of electrolysis; my object was to present a plausible hypothesis and to start my colleagues thinking on these lines.

A paper presented at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 7, 1911, President Wm. H. Walker in the Chair.

THE ELECTROLYTIC SYSTEM OF AMALGAMATING GOLD ORES.

By Elmer Ellsworth Carey.

I am convinced that a revolution in mining methods is imminent, due, to a great extent, to the work of those engaged in research work along electrochemical lines. In submitting this paper, I will have the opportunity to refer to a very valuable paper, read at the December 16, 1910, meeting of the New York Section of this Society, by Mr. John Collins Clancy, on his electrochemical cyanide process. Some comments on Mr.Clancy's paper appear below.

The increasing demand for gold has turned the attention of miners and metallurgists to new fields and new methods, and every year brings down the cost of mining and milling; new extraction methods are being tried, and every effort is being made to save values in low grade and refractory ores. The tailing piles of yesterday are now being reworked; and tomorrow the tailings piles of today will yield further values, as the march of progress discloses new methods, systems and appliances.

The favorite ore of the miner is the so-called "free milling." In such ore the gold particles are comparatively large, and are generally imbedded in quartz ore, free from sulphur, arsenic, etc. Values in such silicious ores may be recovered by the standard system of amalgamation. Then there are other ores where crystals of iron pyrites (sulphides) are found in the quartz, and within the pyritic crystals may be found gold particles in a finely divided state. The values in such crystals cannot be recovered on the usual mill plate, as the particles of gold are coated with various substances, preventing amalgamation. The present practice is to separate the pyritic crystals from the crushed ore by various types of concentrating tables. This so-called concentrate

is then sent to a smelter, or it is ground in tube mills (100-200) mesh and delivered to the cyanide tank, where the extraction ranges from 85 to 96 percent.

Concentrates can only be sent to a smelter where the values are high enough to pay transportation and reduction charges; the cyanide process is expensive and unsatisfactory, unless we admit Mr. Clancy's claim that he has solved the cyanide problems by his system of electrochemical cyanidation.

Another method calls for fine grinding (100 mesh) and electro-amalgamation. An ideal plant for this process consists of some type of rotary crusher, with outside screening, possibly a secondary crushing device to finish the work of the first crusher, and from the crusher the pulp, ground sufficiently fine to release all economic values, is passed over electrolytic amalgamating devices. The released values are recovered in the form of amalgam. Concentration, cyanidation and smelting are unnecessary and the metallurgy of gold is reduced to its lowest terms.

The theory of electrochemical amalgamation has been before the mining world for half a century; one of the earliest authoritative papers on the subject may be found on p. 205, of Vol. I of the *Proceedings of the (London) Institution of Mining and Metallurgy*. Early investigators found as many difficulties as the pioneers in the art of aviation. With no information, no reserve of text book knowledge, no authorities to consult, no works on electrochemistry, it is not strange that the electrolytic method of gold recovery made slow progress. All the problems of current density, anode troubles, forms of construction, etc., had to be laboriously and expensively worked out. To obtain working data regarding the system will cost an independent observer several thousand dollars and a year or two of time; besides he will draw heavily on his stock of good nature, patience and perseverance.

In electrolytic amalgamation, the sole function of the electric current is to deposit hydrogen, sodium, potassium or ammonium in the mercury. The sole function of sodium or potassium is to de-oxidize water, and the final work in the chain of reactions is the liberation of nascent hydrogen at the surface of the mercury. As the particles of gold sweep over the electrolytically excited mercurial surface, all substances usually preventing amalgama-

tion are automatically and almost instantly destroyed or rendered inert. Grease is saponified by the caustic soda; oxide coating on gold particles is reduced by hydrogen; in a word, gold particles are cleaned and amalgamation quickly follows.

It has been known for some decades that in some way amalgamation was intensified in the presence of the electric current; the problem was to devise a machine to utilize the electrical action to the best advantage. Many complicated devices for this purpose have been patented, but as is usually the case, the successful apparatus is simple—almost childishly simple. So simple is the device that extracts all released values, and so broad are the claims made for it, that the builders of our metallurgical temple have persistently rejected this stone. I will follow the scriptural allusion no farther, but I earnestly suggest that in dealing with any difficult extraction problem, the claims of electro-amalgamation be considered.

Hungarian mercury wells are described in Vol. II of Prof. R. H. Richards' Work on Ore Dressing; by making the baffle in such wells an anode, using suitable material, and employing an 8 to 12 volt current of high amperage, we have an electrolytic amalgamating device. The objections to the use of such mercury wells disappear when they are electrified, and their extraction efficiency is greatly increased. The interior of such wells must be lined with some very refractory substances. The ideal amalgamator provides a method by which the gangue is brought closely and intimately into contact with a mercurial surface, which acts as a cathode; provide these conditions, and arrange for suitable capacity and durability, etc., and the low grade and refractory ores of the West soon yield their gold.

Today the mining industry is at a standstill because new conditions call for new methods. The old style mining engineer must give way to the metallurgical and chemical engineer. There are no problems in metallurgy that cannot be solved by the application of the proper electrochemical principles. Electrochemistry has devised profitable methods of extracting the useful metals from other ores, and electrochemistry will also find methods for releasing the noble metals from Nature's refractory grasp. There is more gold in the West than has been mined; lying in plain view in tailing piles, low grade veins, desert sands, beach and river

deposits of the West, there is sufficient gold awaiting the electrochemical engineer to pay the combined national debts of the world. There will be no great advance in the mining industry until the technical schools have furnished a supply of electrochemical metallurgists; for the problems of the mining industry today can only be finally solved by the electrometallurgist.

In Mr. Clancy's paper above mentioned, the author takes occasion to speak rather disparagingly of the electrolytic system of gold recovery. He states: "One of the most severe criticisms on electrolytic processes is where the direct precipitation of the values from the ore pulp is concerned, the objections probably being due to the scouring of the plates by the circulating ore and the consequent loss of finely divided gold amalgam in the ore pulp."

With the use of the electrolytic sodium-mercury cells, as above mentioned, there is no scouring of the plates, and no loss of finely divided gold amalgam; on the contrary, mill pulp after passing the electrolytic sluices, contains only encased values. The aqua-regia test shows no free values. It is true that electrolytic plate amalgamation, to be successful, requires considerable experience in the art, but it is possible to arrange electrolytically excited amalgam plates so that the dire results mentioned by Mr. Clancy do not occur. Electrolytic amalgamation will give extraction results equal to electrolytic cyanidation; and when cost of installation, operation and maintenance are considered, all comparison ceases. Scores of investigators in the last twenty-five years have given testimony as to the efficiency of electrochemical cyanidation; the method of regenerating the cyanide solution and the recovery of values not amenable to straight cyanidation have frequently been referred to in the technical and mining journals. Mr. Clancy deserves credit for calling attention anew to the utility of electrolytic lixiviation, and his standing is such that many engineers will doubtless turn their attention to electrolytic processes. However, I regret that Mr. Clancy should have found it necessary to disparage electro-amalgamation, which is now slowly being recognized by progressive mining engineers as an important factor in milling. But let no one imagine that he can run a few wires from a power line into a solution tank and have a successful electrolytic cyanide plant; and let no one imagine that he

can connect his battery plates with a low voltage generator and thereby greatly increase the extraction. This would be on a par with the village mechanic who purchased working drawings of an aeroplane and set out to build a flying machine.

A simple, but very interesting experiment which may throw some light on the wonderful activity of hydrogen-sodium amalgam and the value of electrolytic amalgamation is made by placing a piece of plastic sodium amalgam the size of a pea in a test tube and adding an ounce of water heavily saturated with ammonium chloride. Test the amalgamating powers of the very curious resultant amalgam by copper and iron wire.

Those who wish to investigate the records of the patent office for progress in electrolytic amalgamation will find the various types of electric amalgamators described in the following U. S. patents:

526,099	579,211	592,793	418,134	370,366
492,711	669,058	548,265	307,081	285,523
641,360	590,524	328,532	757,557	947,958

Copies of the above patents may be had from the Commissioner of Patents, Washington, D. C.

Description of Apparatus.

An electrolytic amalgamating apparatus should be so constructed that there is a constant and regular electro-deposition of sodium (or some similar element) in the mercury, and provision must be made for passing auriferous pulp or sand over the mercurial surface, so that every particle of gold is forced into intimate contact with the mercury. With the automatic deposition of sodium, and suitable mercurial contact, no free values can possibly escape; and the ideal milling plant of the future will consist of some type of rotary crusher producing a 100-mesh product, followed by a series of electrolytic amalgamators. Such an arrangement will extract all values shown by any free gold test.

The ideal electrolytic amalgamator consists of a series of electrolytic sodium-mercury cells, followed by another electrolytic amalgamating device in which the values are recovered on silver-

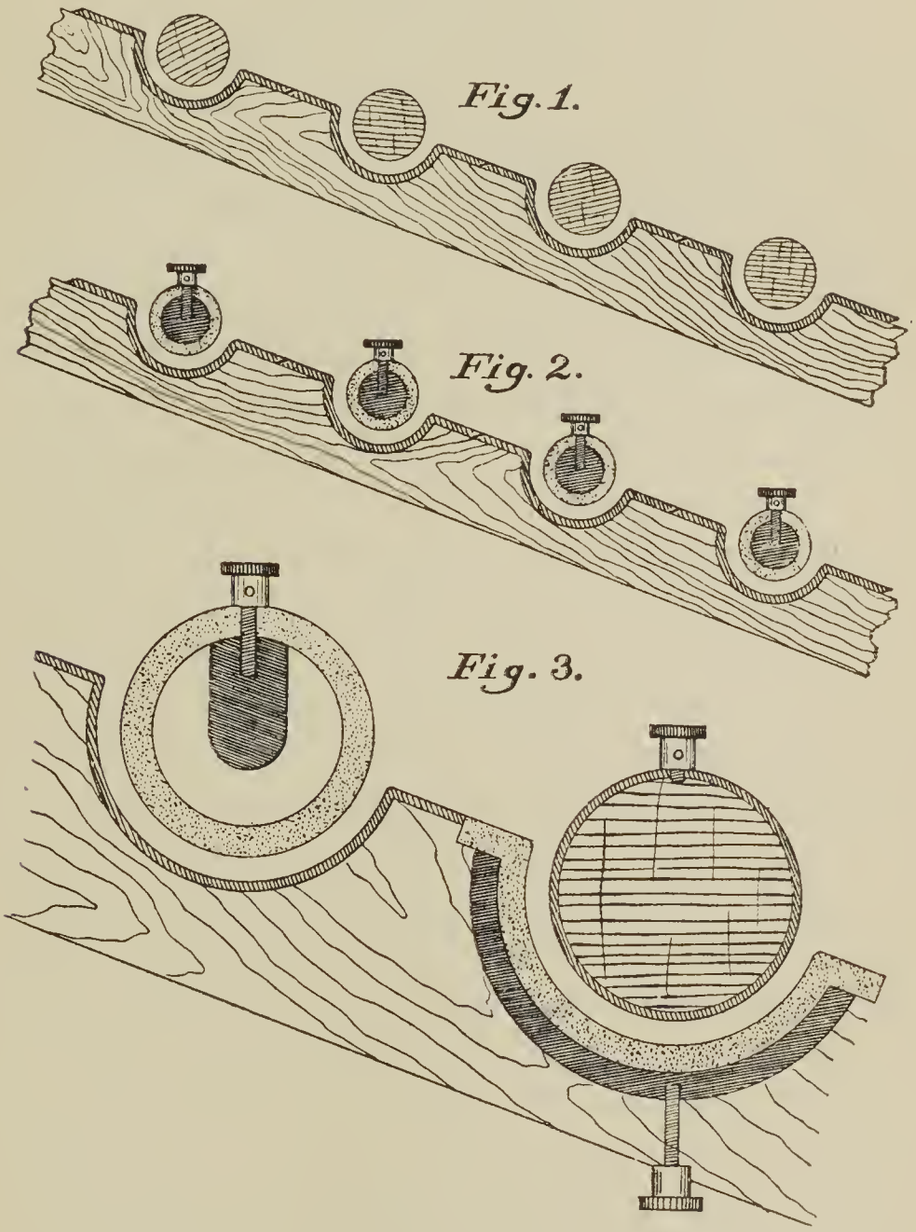
plated copper plates, of suitable construction. With the mercury wells, high amperage may be employed, liberating large volumes of hydrogen, which removes all coatings (oxides, sulphides, grease, talc, silicious coatings, etc.) from the microscopic gold particles; in the secondary amalgamator the plates offer a large cathode area so that all portions of the pulp are forced into contact with a highly active mercury surface. The supplementary amalgamating device above mentioned consists of a silvered copper plate of suitable width; this plate contains parallel, transverse, semi-cylindrical depressions (grooves, pockets or riffles) the full width of the plate; into these grooves project cylindrical terra cotta cylinders, leaving a quarter-inch clearance, from three to four inches in diameter; these cylinders contain a graphite core, one inch in diameter, connected as an anode.

The pulp passes under the cylinders, and sweeps gently over the curved (cathode) amalgam plate, while gravity, the force of the water and centrifugal force tend to drag each gold particle into contact with the highly excited mercury surface. With such a series of amalgamating riffles, supplied with a low voltage current of proper density, we have an amalgamating device of wonderful activity. It is not too much to say that this simple device will extract 99 percent of the values which may be saved by any system of lixiviation, the cost of extraction being insignificant.

Fig. 1 shows a section of a new type of mill plate which I have devised. The sides are not represented. The silver-plated copper plate (being of the usual length of amalgamating plates) contains transverse parallel semi-cylindrical grooves into which fit solid cylindrical wooden baffles; these baffles may also be made of standard piping or casing, from three to four inches in diameter, with the ends closed. The clearance between the plates and the baffles is from three-sixteenths to one-quarter inch. One piece of copper plate may be used, with the proper depressions pressed therein, or, preferably, a number of overlapping plates may be used, each plate containing one or two semi-cylindrical depressions. The plates are held in position by their own weight, fitting closely to the sides, and can be quickly removed from the device for cleaning up. The device may be given any desired grade, and the plates are dressed and operated as the usual mill

plate. A mill plate arranged as described will make a better extraction on the average ore than the usual type of amalgam plate, there being no loss of amalgam.

In Fig. II is illustrated an electrolytic mill plate, constructed similarly to the one shown in Fig. I, which will not only recover



all values saved by the standard types, but in addition, all free values in silicious pulp and slimes, all values in placer material, beach-sand and all black-sand values are also recovered. The cylindrical baffles are made of terra cotta, and each contains a graphite core connected to the positive lead of a low voltage generator; the amalgam plates are connected to the negative lead of the generator.

In the first groove or riffle shown in Fig. III, the water and pulp passes over the amalgam plates as in Fig. II; in the second riffle of Fig. III, the amalgam plate, connected to the negative lead forms a casing for the baffle, and the pulp stream passes *under* the mercurial surface, thus bringing the surface of the water into intimate contact with the electrically excited mercurial surface; or a copper cylinder, silver plated, may be used as a baffle, and at the same time act as an amalgamating surface. A gold saving device may consist of a series of such riffles as shown in Fig. III, arranged alternately; such an arrangement is particularly useful in treating pulp containing gold in a finely divided form, or for recovering values in slimes or in solutions. By screening placer material to 10 or 12 mesh, and passing the undersize over an electrolytic amalgamating sluiceway of suitable length, all fine, rusty, float, coated and greasy gold is recovered.

With the standard system of mill-plate amalgamation, many difficulties are encountered; with the device just outlined, all the usual amalgamation troubles disappear. The plates may be dressed by hand in the usual manner once a day; by adding a mercuric solution to the water, the proper amount of mercury will be deposited electrolytically to keep the plates in excellent condition. Electrolytic sodium amalgam containing gold is soft, yet tenacious; it is plastic and arrests every particle of passing gold, yet such amalgam never crumbles. Such an apparatus will extract free gold from material having any kind of gangue, clayey, sulphurous, arsenious, etc., and there is no fouling, no formation of sulphide coatings, no discoloration by tellurides, arsenides, etc.

In certain classes of base ores it may be necessary as a preliminary measure to treat the pulp for 30 minutes by electrolytic pan amalgamation before passing the pulp over the electric sluice; and for ores containing gold in chemical combinations (sulpho-tellurides, etc.) a preliminary roasting may be required.

In the near future we may look for a greatly increased production of gold, due to the application of electrochemical methods in mining and milling operations; were electro-amalgamation and electro-cyanidation today in general use in other mills now in operation, the gross output of gold would be increased 25 percent. The great increase in the future supply of gold, however, will come from vast low-grade deposits and ledges which cannot now

be economically mined. A new field containing fabulous treasures awaits the command of the modern Aladdin—the electrochemical engineer.

DISCUSSION.

DR. N. S. KEITH: The idea is an old one, at least so far as H is concerned. The use of sodium amalgam is no longer practiced on a commercial scale. The sodium readily reduces metals other than gold, and keeps them from oxidizing; for instance, the fine particles of iron from wear of the stamps or other grinders or pulverizers. These, when bright, are readily amalgamated; but when current ceases and the sodium is hydrolyzed, the base metals in the mercury oxidize and rise to the surface, forming a foul scum.

MR. E. E. CAREY (*Communicated*): It is true that iron and other free metals have an affinity for sodium amalgam, as Dr. Keith remarks, and the oxide coatings will form on the mercury surface when the electrochemical action ceases. It is possible that some, not familiar with the subject under discussion, might assume from the facts noted that electrolytic amalgamation was impracticable.

The presence of basic oxides does not seriously interfere with the amalgamating process; when there is an excessive accumulation of base oxides, the mercury can be drawn from the riffles to a tank, where the oxides will rise to the surface, and the mercury drawn from the bottom of the receptacle will be free from oxides.

By a very simple device, the mercury in the first set of riffles can be automatically and continuously withdrawn, freed from oxides, and returned to the amalgamating sluices. In the electrolytic amalgamating sluice where values are deposited on amalgam plates, there is no formation of oxide coatings, as such oxides are carried away by the passing water and pulp as soon as formed, and the mercurial surface is at all times free from foul conditions.

It may further be noted that a mercury surface which will

amalgamate iron will retain any particles of free gold which come in contact with it, regardless of the chemical conditions; and as the prime object of mining processes is to recover gold, any process which will recover all the precious metals is worthy of serious consideration, even if an allowance for base metals is found in the bullion returns. Far better some iron in the amalgam than some gold in the tailing piles!

It should be remembered that electrolytic amalgamation may be accomplished by three separate methods:

1. By electro-pan amalgamation, where the pulp is gently agitated over a mercury bath for the required time; by continued treatment and heavy current density, the most refractory coatings may be removed.

2. By the electrified Hungarian mercury-riffle.

3. By a series of electrified amalgam plates.

These methods may also be combined to meet varying conditions.

A paper read before the New York Section of the American Electrochemical Society, on December 16, 1910; and called up for further Discussion at the Nineteenth General Meeting of the Society, New York City, April 7, 1911. President Wm. H. Walker in the Chair.

THE CLANCY ELECTROCHEMICAL CYANIDE PROCESS.

By John Collins Clancy.[1]

This process is more immediately concerned with the treatment of refractory ores, these ores generally having their values associated with compounds in chemical combination, which are not susceptible to the action of solvents until roasting or some other method of oxidation has disassociated the said compounds and liberated the precious metals. Roasting is by all means the cheapest oxidation process so far known, any attempt to oxidize the base constituents by other chemical means is obviously of a very expensive nature, therefore, commercially impracticable. It is known that, in some cases, profitable extraction of the precious metals from base ores may be obtained, depending on how rapid the action of the cyanide is upon the finely divided gold in preference to its action upon the base constituents, that is to say, before the base metals are attacked the gold has been dissolved. Sometimes by keeping down the alkalinity of the solution to an almost neutral point in "protective" alkalinity, a good extraction may be obtained, as the absence of an excess of alkali will protect the metallic sulphides from decomposition and allow the cyanide to work directly upon the precious metals. Of course, these results are only capable of accomplishment when the precious metals are not in chemical combination, unless a solvent for the chemical compounds is present with the treatment solution. The Clancy process in a measure includes the embodiment of these principles.

As a preamble, a little history relating to my earlier experiments on refractory ores may not be out of place. The ores of Cripple Creek, Colorado, may be taken as an example of so-called refractory ore. I need not dwell upon the past or present metallurgical treatment of these ores, but will only state in passing,

[1] Consulting Technologist of the Moore Filter Co., New York City.

that straight cyanidation of the raw undressed ore yields but a trifle over 60 percent extraction. It will be apparent, therefore, that a process to extract from about 90 to 95 percent of the values without roasting or concentration, and at a reasonable cost, would be a boon to the district of Cripple Creek, as well as to other similar districts in different parts of the world. To this task I set myself some years ago, and my improvements may be seen from reading the different specifications, which show my line of thought and gradations from earlier processes.

The object of my first experiments on Cripple Creek ores was to find a cheap alkaline solvent for the telluride of gold which occurs in these ores, the tellurides existing principally in the form of (AuAg) Te_2; the mineral calaverite and sylvanite may be approximately represented by this formula. The minerals calaverite and sylvanite are often found alone, but more frequently associated with pyrite; this close association with the pyrite increases the difficulty of treatment by chemical solutions as well as separation by mechanical means.

I discovered that the alkaline hypochlorites, hypobromides, hypoiodites (NaClO) (NaBrO) (NaIO) dissolved tellurium readily and also attacked the tellurium in the gold telluride compounds, while their calcium salts—the analogues of bleaching powder, were not solvents. Sodium hypochlorite being the cheapest, there was therefore a possibility that by crushing the ore fine the tellurium would be dissolved off, and allow solution of gold by cyanidation. The equation representing this reaction may be as follows:

$$Te_2 + 4NaClO + 2H_2O = 2H_2TeO_3 + 4NaCl$$

the tellurous acid so formed would dissolve in the excess of alkali—

$$H_2TeO_3 + 2NaOH = Na_2TeO_3 + 2H_2O$$

A preliminary treatment with NaClO followed by a cyanide treatment on ore crushed to 100 mesh, invariably gave an extraction of from about 80 to 85 percent of the gold contents, and frequently a higher extraction when the gold telluride in the ore was not closely crystallized with the pyrite. The preliminary treatment, however, had its drawback, inasmuch that the remain-

ing NaClO left in the pulp after treatment destroyed cyanide unless washed out entirely, this washing caused extra filtering, and meant two sets of solution treatments, and for that reason, together with the alleged high cost of producing NaClO, the test was not continued.

My next process was the employment of a soluble persulphate, such, for example, as ammonium persulphate, as a preliminary treatment to dissolve the tellurium contained in the ore. This solvent, $(NH_4)_2S_2O_8$, was superior to NaClO, owing to the fact that the iron sulphides did not become oxidized to any appreciable extent while the tellurium was undergoing solution. Another advantage—the remaining persulphate did not act to destroy the cyanide on subsequent treatment; on the contrary, it hastened solution of the gold, after the following equation:

$$4KCN + 2Au + (NH_4)_2S_2O_8 =$$
$$2KAu(CN)_2 + (NH_4)SO_4 + K_2SO_4$$

The high cost of the persulphate, together with the necessity of using two sets of solutions, was the reason for not continuing this method. I next tried if it were possible to dissolve the tellurium and gold simultaneously by using a mixture of cyanide and persulphate. This scheme was found to work satisfactorily on gold telluride crystals, but when applied to the ore, the method was prohibitive on account of the large amount of persulphate required, due principally to the presence and formation in the solution of ferrocyanide, which caused the action of the persulphate to be completely nullified. The thought then occurred, could some substance be used to prevent the action of the ferrocyanide upon the persulphate. Reflecting on the behavior of the alkaline hypo-halogen compounds towards KCN, I recalled the weak action exhibited by sodium hypoiodite upon KCN in comparison to that exhibited by sodium hypochlorite and sodium hypobromite; the latter compounds almost immediately converted the KCN into KCNO in alkaline solution—in acid the solution formed cyanogen bromide and cyanogen chloride, respectively. Guided by this process of thought, the idea of using a soluble iodide, together with the persulphate in the cyanide solution, at once suggested itself, and I forthwith tried the effect of potassium

iodide in conjunction with persulphate and cyanide solution, on gold tellurides, with the result that the tellurides underwent complete solution. The nature of the reaction at once explained itself—there being no alkali present in any of these tests, other than the alkali occasioned by the hydrolysis of the cyanide solution, it was simply the persulphate liberating the iodine in presence of the cyanide solution to form cyanogen iodide. The following equations may represent the action shown in two stages:

$$2KI + K_2S_2O_8 = 2K_2SO_4 + 2I$$

then

$$2I + KCN = ICN + KI$$

From the study of these reactions I conceived the idea of liberating iodine while the ore was in contact with the cyanide solutions, by the use of a substance yielding nascent oxygen, using any oxidant which had not a too high velocity reaction, and one which did not unduly increase the alkalinity of the solution so as to prevent the formation and existence of cyanogen iodide in the said solution. Persulphate apparently filled these conditions, as it introduced no free alkali while giving off nascent oxygen, but, on the contrary, neutralized alkali, owing to its anxiety to part with one of its sulphions (SO_4)

$$K_2S_2O_8 + 2KOH = 2K_2SO_4 + H_2O_2$$

It will be seen from the above description that the solutions would contain free cyanide together with cyanogen iodide and the oxidizing agent—persulphate, the proportion of cyanogen iodide to cyanide depending upon the speed of the reaction and ratio of persulphate to potassium iodide. To apply this solution to the treatment of ore and maintain the chemical equilibrium necessary for producing cyanogen iodide required very skilful manipulation. For example, the ore had to be made alkaline by applying the necessary protective alkali to the cyanide solution; if excess of alkali was added, the persulphate would still liberate iodine, but the iodine so liberated immediately formed alkaline hypoiodite; the hypoiodite formed was rapidly destroyed by the sulphides contained in the ore, thus rapidly using up the oxidizing energy of the oxidizing agent. The amount of alkali to be added depended, first, on the acidity of the ore; second,

on the proportion of persulphate added, the persulphate requiring alkali in proportion to the removal of its (SO_4); third, the influence of time on the rate of progress of the reaction; fourth, the influence of atmospheric oxygen during agitation, accelerating the oxidation of sulphides, which developed acidity and required alkali. To control this alkalinity, sufficient alkali had to be added, but not enough to destroy the cyanogen iodide; again, the cyanogen iodide formed would, in the presence of alkali and sulphides, form sulphocyanides, representing a direct loss of cyanide. Nor is this all; when the agitation treatment was completed, the solution, after leaving the ore, preparatory to filtration, would drop, *i. e.*, show a greater cyanide consumption than when in contact with the ore. This consumption of cyanide was probably due to the cyanogen iodide formed, together with the remaining persulphate, acting upon the cyanide solution in absence of the retarding influence of the reducing agents in the ore. When it was necessary to add alkali to the solution in order to secure the proper precipitation in the extractors, a further consumption of cyanide took place after the equation:

$$CNI + 2KOH = KCNO + KI$$

I discovered that this consumption of cyanide could be completely stopped, and the cyanide which had combined to form cyanogen iodide, regenerated, by the simple addition of sodium sulphite (Na_2SO_3) and lime after the equation:

$$CNI + Na_2SO_3 + H_2O = NaCN + NaI + H_2SO_4$$

The lime added neutralized the acid produced. The addition of sodium sulphite acted perfectly at this point, but it did not take care of the decomposition of cyanogen iodide to alkaline cyanate produced by the necessary presence of alkali in the ore treatment process (a measure, of course, not allowable in the treatment tank). It is obvious that the above process would require a skilled manipulator to obtain results at a reasonable cost; in a word, the process is not foolproof. However, if the market price of persulphate would drop to a reasonable figure, and cheap salt used which would undergo hydrolysis, *i. e.*, give hydroxylions in solution to the extent of taking up the acidity produced by the oxidation means employed, then the process

would require no more attention than the ordinary straight cyanide process.

Ozone as an Oxidizing Agent.

In view of the high cost of persulphate, my attention naturally turned to the use of a cheaper oxidizing agent and one that would not introduce, as before stated, alkali in the solution. Ozone, therefore, claimed my attention, as previous experiments with ozone gave interesting results, and as there were several ozonizing machines on the market at this time, I began to look around for the most economical machine which produced the greatest amount of ozone at the lowest cost. One machine in particular was guaranteed and backed up by a reputable, well-known firm to produce from 100 to 150 grams of ozone per kilowatt hour, and figuring the cost of electrical energy at one cent per kilowatt hour, it seemed that I had now struck the right nail on the head as regards a cheap oxidizer. An ozonizer of the above description was immediately purchased and installed in my laboratory, whereupon I at once set to work to test the action of the ozone on the treatment of ores with cyanide solution containing soluble iodides, using the ozonized air produced by the ozonizer to liberate the iodine from the necessary chemicals while in contact with the ore. It would take up too much space to give in detail the results of the numerous tests made on different samples of ore; in short, the ozonized air acted as a first-class oxidizing agent and gave excellent results. The only thing against this scheme was that it consumed too much cyanide, unless very carefully watched, it being difficult to establish the proper equilibrium necessary to prevent rapid oxidation to cyanate. The equation representing the action of the ozone upon the iodide was as follows:

$$O_3 + 2KI + H_2O = O_2 + 2I + 2KOH$$

and, of course, the iodine combined with the cyanide to form cyanogen iodide, as already shown in one of the foregoing equations, the excess ozone forming with the cyanide KCNO after the equation:

$$O_3 + KCN = KCNO + O_2$$

The question now was how to prevent this formation of KCNO.

Learning from previous tests on ores containing large amounts of reducing agents that the consumption of cyanide was not so great as with ores which did not contain reducing agents, the thought suggested itself to add a reducing agent to the cyanide solution. I knew that potassium sulphocyanide, although in a sense a reducing agent, had no action on straight cyanide treatment, *i. e.*, the atmospheric oxygen was not absorbed by it. Experiments showed that when sulphocyanide was subjected to ozonized air, cyanide was generated after the equation:

$$KCNS + H_2O + 3O_3 = KCN + H_2SO_4$$

The alkali present of course neutralized the acid as produced, and the cyanide so formed was not decomposed as long as the sulphocyanide was present. This action opened up a field for thought, and in following it, I tried the action of ozonized air on sulphocyanide solution containing an iodide. Upon introducing the ozonized air into the vessel containing the sulphocyanide and the iodide solution, free iodine was at once liberated. When this experiment was repeated, using part of the same original solution, but with a small addition of alkali, on again passing the ozonized air through the mixture the solution immediately assumed the characteristic iodine coloration. This solution was exceedingly active on gold leaf and on telluride of gold, presumption being that the solution contained cyanogen iodide and free cyanide. The formation of cyanogen iodide by this means may be represented by the equation:

$$3KCNS + 3KI + 4O_3 = 3ICN + 3K_2SO_4$$

Following up this discovery, as shown by the foregoing equations, I proceeded with my tests, using the sulphocyanide to prevent the direct formation of cyanate, and was rewarded with most satisfactory results, the consumption of cyanide being very much reduced. However, the amount of cyanide consumption which did take place over and above that consumed by the ore as compared with straight cyanide, was probably occasioned by the cyanogen iodide formed being oxidized slowly to cyanate in presence of alkali. The speed of this reaction was not great, and probably occurred after the following equation:

$$5CNI + 6KOH = 5KCN + KIO_3 + 2I_2 + 3H_2O$$

Potassium hypoiodite (KIO) being formed as an intermediate product, the excess of iodine acting upon more alkali forming hypoiodite would destroy the KCN formed and eventually become oxidized to KCNO.

Here was a field for the expansion of the process on the large scale, but there is always a "but." While the production of ozone was apparently cheap enough as regards the cost of electrical energy, the cost of the machine (installation) to produce enough ozone to treat, say, 1,000 tons of ore per day was staggering. The machine required the supervision of trained experts, and for a 1,000-ton-a-day plant, a battery of about 500 unit ozonizers would have been required, besides various other mechanical objections too numerous to mention. "Another hope blasted!"

The production of ozone by electrical means is yet in its infancy, and it is only within the last few years that ozonizers have been put on the market to give ozonized air of high concentrations. In the very near future it is probable that ozonizers will be built to give large volumes of ozonized air at high concentration with a small installation of ozonizer units. Meanwhile I had to look around to find a substitute. How was it to be found? I had already exhausted almost the whole list of economical oxidizers known to chemistry.

Electrolysis.

The employment of the electric current claimed my attention as a means of producing the oxidation necessary while the solution was in contact with the ore. Electrical means for the treatment of ore labors under a stigma, inasmuch as there have been many unfavorable criticisms on the use of electrolytic processes, no doubt caused by the numerous failures. Among these may be mentioned the electrical precipitation of gold, requiring the installation of an enormous plate surface, electrode difficulties, and the consequent destruction of the cyanide by the use of the current. One of the most severe criticisms on electrolytic processes is where the direct precipitation of the values from the ore pulp is concerned, the objections probably being due to the scouring of the plates by the circulating ore and the consequent loss of finely divided gold amalgam in the ore pulp. Much more

could be said on this subject, but the Clancy process is not concerned with any electrolytic amalgamating process, nor deposition of the gold on plates, nor upon the dynamical theory of the gold being brought against the cathode electrode and there meeting with nascent hydrogen, nor the ore being brought against the anode electrode and meeting with the nascent oxygen. The process thus differentiates itself into a method of using the electrical energy to disassociate the chemicals employed, and by their agency doing the necessary work.

Electrodes.

It will be obvious from the foregoing that the use of electrolytic methods requires proper anodes. Numerous substances to act as anodes have been tried, such, for example, as lead peroxide, carbon, iron, graphite, etc., all these substances having been more or less inefficient. Anodes of lead peroxide under the influence of high current densities break down, *i. e.*, disintegrate. Iron when used as an anode is oxidized by the nascent oxygen liberated, and forms hydrated oxides of iron, and should the cyanide solutions contain halogen salts, the corresponding iron halogen compounds are formed. It is needless for me to describe the many difficulties which I have been up against to find a suitable anode. All the common metals, together with different alloys and compounds, were experimented upon to find a substance which would withstand the action of the halogen compound, *i. e.*, some substance that would not combine with either chlorine, bromine or iodine under the action of the current, so as to allow the liberated halogen or the nascent oxygen to do the useful oxidation work in the solution.

Graphite (extruded) stands the electric current fairly well, *i. e.*, makes a good anode while it lasts, but under the influence of high current density it disintegrates and cannot be used for any length of time in circulating solutions containing ore in suspension, as it is worn away by the attrition or friction of the ore particles against the said electrodes. Nor is this all. When it is understood that graphite will not stand a much higher density, say, 10 amperes per square foot of surface, it requires no calculation to figure out the amount of electrode surface required on a working scale. The only metal which would stand

up under the electrolysis of cyanide-bearing solutions containing halogen compounds was platinum. On a commercial scale the employment of platinum could not for one moment be entertained.

After trying out every known electrode which I thought might prove suitable, I found that oxide of iron which had been melted in the electrode furnace was the only thing that would stand up under high current densities and not combine with the halogen compound contained in the cyanide solution. The area of anode surface of this material to give the necessary current density is reduced to a fraction of the amount of surface required in the case of graphite. In general, these melted iron oxide electrodes used, as described, are particularly suitable for the electrolysis of cyanogen-bearing solutions, and present the following advantages over all other anodes, including platinum: First, they are cheaper, and they have an unlimited life in comparison with the other anodes already mentioned; second, they furnish nascent oxygen free from carbonic acid, which is of great advantage in the electrolysis of cyanide solutions; third, they do not disintegrate under high current densities, and are so hard that they do not wear away by the attrition of the ore pulp in the agitating tank.

Armed with the necessary weapons in the shape of these highly inert refractory electrodes, and with confidence in my process based on previous experiments with platinum electrodes, I felt sure that I could accomplish anything in the shape of electrolysis of cyanogen-bearing solutions containing halogen compounds. I could now use high current densities and liberate chlorine, bromine or iodine in the said solutions without worrying about my anode breaking down. It will be remembered in my earlier experiments that I was confined to the use of persulphate, together with iodine or soluble iodide, as no other oxidizer, not even ozone, would liberate bromine or chlorine in the alkaline cyanide solution. Taking advantage of these new-found electrodes, I experimented with cyanide, sulphocyanide and a soluble bromide, and obtained excellent results on the most refractory ores by keeping the solutions at the neutral point, so as to allow of the formation of bromo-cyanogen while in contact with the ore. The use of a bromide as above described, although giving results equivalent to the use of soluble iodide, was more difficult

to control, owing to the necessity of maintaining the solutions at the neutral point, and required more electrical energy to do the same work as iodide. Again, by keeping the solutions at the neutral point, the formation of cyanate was much more rapid, consequently the free cyanide did not coexist very long in the presence of the cyanogen bromide, owing to its high speed of reaction. The bromates produced by the oxidation action would accumulate in the solutions and were apparently not reduced to bromides even after passing through the zinc boxes. In the case of using a soluble iodide, any iodates formed were at once reduced by the action of the sulphocyanides. This reaction between sulphocyanide and an iodate is very striking, so much so that if we take a solution of an iodate and add to it a solution of sulphocyanide, on acidifying this mixture, immediate liberation of iodine takes place; or, again, if we take a solution of iodate containing sulphocyanide and electrolyze the same, iodine is immediately liberated at the anode. With bromates this is not the case. Bromates are reduced more or less by the nascent hydrogen evolved at the cathode. But this nascent hydrogen has to do other work; in fact, it has no time to look after the complete reduction of bromates, as during electrolysis a thin pellicule of calcium hydrate is produced on cathode. The formation of this pellicule is occasioned by the presence of calcium salts in the solution. This pellicule scales off, but is immediately reformed, thus more or less preventing the hydrogen gas in its atomic state from coming into contact with the electrolyte and causing a union of the atoms to molecular hydrogen. When the hydrogen has once assumed the form of molecules, then its reducing power is at an end. Bromates, therefore, have a chance of partial reduction in the treatment tank. The advantages possessed by the use of iodine over bromine are the following: Iodine is easily liberated from its compounds at a very low voltage; it does not react violently upon the cyanide solution; it is continuously reduced from its higher oxidation state by the sulphocyanides present in the solution; it can be liberated from its compound in alkaline solutions—this fact prevents the loss of valuable iodine due to volatilization. The fact that iodine forms cyanogen iodide in a slightly alkaline solution is of extreme importance in the treatment of ores, as by this fact sufficient

free cyanide coexists during the formation of cyanogen iodide. The decomposition of cyanogen iodide to cyanate in the presence of alkali takes place slowly, thus allowing ample time for the precious metal's dissolution.

This method of using cyanide sulphocyanide and a halogen compound in conjunction with the electrolysis of the solution gave excellent results on most of the so-called refractory ores. The cyanide could have been regenerated from the KCNS (*i. e.,* the KCNS which had formed due to the action of the cyanogen iodide upon the sulphides during treatment) but for the presence of the halogen compound.

The reaction:

$$KCNS + 3O + 2KOH = KCN + K_2SO + H_2O$$

takes place only to a limited extent. The presence of the halogen salt handicapped this reaction, *i. e.,* it finally became more or less a reversible one after the following equations:

$$KCNS + KI + 2KOH + 4O = KIO + K_2SO_4 + KCN + H_2O$$

$$KIO + KCN = KCNO + KI$$

$$KIO + KCN + K_2S = KCNS + KI + K_2O$$

In a word, the formation of KIO oxidizes the KCN to cyanate, and when regenerating the solution in the presence of ore, the KIO acts upon the sulphides in the presence of alkali, producing KCNS. It will be seen that it is difficult to establish the correct ratio of alkali to obtain an equilibrium to allow of the formation of KCNS and prevent the formation of cyanate. How could this formation of cyanate be prevented? How could the cyanogen-bearing solution be regenerated? Numerous experiments made with all kinds of additions, conducted upon scientific principles, with a view to reducing the cyanate to cyanide, gave most discouraging results. As far as I am aware, there is no record in technical literature in reference to the regeneration of cyanide from solutions of cyanate; therefore I had to launch out into a sea of speculation. My first experiment was to try the action of the electric current upon a chemically pure solution of potassium cyanate. The action of the current upon straight cyanide (as is well known) results practically in the formation

of cyanate. I therefore tried the effect of continued electrolysis upon a pure solution of KCNO. It was not my intention to chase any scientific butterflies, but only the question as to what were the products of electrolysis. I forthwith proceeded with my experiment. On examination of the cathode product, NH_3 revealed its presence by its action on the olfactories. At the anode I collected CO_2, the solution meanwhile increasing in alkali. These products for a start were by no means encouraging. However, as a preliminary to an intended systematic research and to see if there was any possibility of some reduction to cyanide, I withdrew a portion of the liquid from the containing vessel and floated some gold leaf upon the surface of the solution, and set it aside for observation, meanwhile continuing electrolysis of the remaining solution. After about ten minutes, this solution became very hot. I was about to throw it out as a spoilt experiment, but, thinking there might be some intermolecular change due to the increased temperature (having in mind, amongst other things, Wohler's discovery, *viz.*, conversion of ammonium cyanate into urea), I withdrew a second portion of the solution and floated gold leaf upon its surface, placing it alongside the first experiment. I watched both solutions carefully. No. 1 experiment, which had already stood fifteen minutes, showed no signs of dissolving; No. 2 experiment, after ten minutes surprised me, for the gold was surely being dissolved, and in thirty minutes it was completely dissolved. No 1 experiment after standing all night showed no signs of dissolution. Thinking that the reason why No. 1 did not dissolve gold leaf was owing to its not having the same amount of current as No. 2, I set to work and made two experiments under precisely the same conditions, with the exception that one was kept cold by immersion of the containing vessel in a freezing mixture, while the other one was allowed to become warm as before. After giving both the same ampere hours of electricity, I floated gold leaf on each solution. On thirty minutes' standing, the one that was allowed to become hot dissolved gold leaf completely; the one which was kept cold showed no signs of dissolution even after three days' standing. Platinum electrodes were used in both experiments. What was the cause of the difference between the electrolyzed hot and cold solutions? Was it the formation of urea? I at once electrolyzed

a solution of potassium cyanate containing a small portion of urea, adding a small amount of caustic soda to increase the conductivity. By this means the solution kept at about room temperature. On completion of electrolysis, gold leaf was floated upon the surface of this solution and allowed to stand to await results. In about fifteen minutes the gold leaf underwent complete solution. From this it would appear that the urea theory was probably correct, or was it the cyanate in conjunction with the urea, together with the action of the electric current-producing cyanide, isopurpurate, or some other gold-dissolving compound? Testing with silver nitrate showed apparently considerable quantity of KCN, but nothing commensurate with its dissolving value on gold leaf.

Discovery of Action of Cyanamide.

Having made this discovery, that urea in conjunction with the cyanate and electrolysis of the solution dissolved gold leaf, the next question was: Would any similarly constituted organic compound do the same thing? Urea being an amide compound (carbamide), I at once thought of cyanamide. I thereupon added a solution of cyanamide (using the calcium cyanamide of commerce, which is soluble to the extent of about 58 to 60 percent in water) to a cyanate solution, electrolyzed same, and treated the solution as before with gold leaf; dissolution of the gold took place in a few minutes. With a view to studying this peculiar reaction, I tried the action of electrolysis on a solution calcium cyanamide. Without any other admixture other than the addition of a little alkali to increase the conductivity, after electrolyzing for ten minutes at a fairly high current density, the solution dissolved gold leaf in about fifteen minutes. This solution also gave a substantial titration with silver nitrate, showing probably that cyanide had formed. Again treating the original solution with the addition of potassium thiosulphate, and boiling for the purpose of converting any cyanide present into sulphocyanide, on testing this solution with ferric chloride, it gave the characteristic blood-red coloration of the iron sulphocyanide—surely ample verification; but to make it more confirmatory, I added a solution of ferrous sulphate to convert any cyanide in the solution into ferrocyanide. On addition of ferric chloride, it gave, on boiling,

the characteristic Prussian blue. I was therefore satisfied that some cyanide was formed by the electrolysis of calcium cyanide, but as to the amount produced from a given quantity of cyanamide, I was in the dark, owing to the peculiar behavior of the titrating solution in presence of organic compounds. It seemed, from different experiments made, that the production of cyanide by electrolysis of cyanamide solution frequently never rose above 0.3 to 0.4 pound KCN per ton of solution. During all these tests, I used solutions of analogous strength to working scale practice. On referring to Watt's Dictionary of Chemistry, Vol. II, page 314, line 65, it is stated, in substance, that cyanamide combines with potassium cyanate to form mono-potassium amidodicyanate, formula $(CN)_2NH_2OK$. Reflecting on this reaction, I thought probably that, as the cyanide was formed by the electrolysis of the cyanamide, it was oxidized by the current to cyanate, the cyanate then acting upon the unaltered cyanamide to form potassium amidodicyanate, and potassium amidodicyanate, when electrolyzed, forms a powerful gold solvent, although it does not give any appreciable titration with silver nitrate. It will be, I trust, appreciated that to go into discussion of these reactions would not only require an enormous amount of space, but prove too severe a tax upon my time; suffice it for the present to say that I have a number of notebooks filled with interesting data in regard to these reactions, showing how they branch off and become diversified. I therefore propose later on to publish the results of the different experiments and theory relating to the data of my notebooks.

To go into practical work is more to the point of this article. However, before leaving the theory, which is always the necessary scaffolding for building up an edifice, I may state that when a solution of calcium cyanamide is mixed with a solution of alkaline ferro cyanide and allowed to stand for a few hours, and even after weeks of standing, it becomes an active solvent for gold, and without the aid of electrolysis, and when applied to the treatment of ores amenable to straight cyanidation, gives results equivalent to the simple cyanide treatment, even in very dilute solutions.

Further, this process can be used on ores which have already been treated by the cyanide process, that is to say, on the residues

commonly known as dumps. There exists in these dumps a large proportion of Prussian blue, which, when treated with alkali, becomes in substance potassium ferro and ferri cyanide, or soluble prussiates.

This opens up a cheap means of treating ores amenable to the ordinary cyanide process as well as ores (residues) which have already been treated by the cyanide solution; that is to say, ores from which the precious metals have not been wholly extracted, and which would not pay for re-treatment by the ordinary cyanide process on account of the cost of cyanide.

The following is an example of using this process upon ore amenable to cyanide treatment:

Take 2,000 pounds of water containing 1 pound of calcium cyanamide, 1 pound of alkaline ferro-cyanide and 1 pound of lime. The ore is subjected to this solution in the ordinary way, say, in proportion of two parts of solution to one part of ore, for a period of, say, eight to ten hours, or until extraction is complete.

The following is an example of using the process upon ore which has already been treated by the cyanide process and exposed to atmospheric oxygen, which occasions the formation of Prussian blue and other ferro cyanogen compounds.

This ore, when treated with a solution containing 1 pound of cyanamide, 1 to 5 pounds of lime (the amount of lime, of course, depending upon the acidity of the ore), in 2,000 pounds of water, gives results equivalent to the use of straight cyanide solution when used in the proportion of two or three parts of solution to one part of ore.

Again, if the above mixture is electrolyzed, the solution of the gold is extremely rapid. Calcium cyanamide mixed with alkaline sulphocyanide, electrolyzed, immediately becomes cyanide, and dissolves gold rapidly. To show the action of another amide compound, for example, guanidine carbonate mixed with potassium cyanate, in conjunction with electrolysis of the solution, dissolves gold leaf in less than ten minutes. I might go on here and cite a whole list of amidogen compounds in conjunction with cyanate solution, if space would permit, and I have no doubt it would be interesting to those following this subject.

In the midst of this work on cyanogen-bearing materials, the thought occurred to try the combination of calcium cyanamide

and iodine. I forthwith made a solution of calcium cyanamide, adding a solution of iodine to see if this combination would dissolve tellurium, and was rewarded by finding it to be an excellent solvent. I next tried gold leaf on the same combination, and had the satisfaction of seeing the gold go into solution in a short time. A scum of calcium carbonate forms on the surface, preventing more rapid solution. From this I deduced that the addition of iodine formed cyanamidogen iodide. I am unable to find any reference to this compound in chemical literature which I have read, and I therefore take the liberty of calling it by the above name, and further presume the formula to be CN_2I_2. I next tried the action of cyanogen iodide upon a solution of calcium cyanamide, and, knowing that cyanogen iodide would be destroyed by an excess of alkali, anticipated that this combination would dissolve telluride of gold. Upon applying the solution to tellurium and telluride of gold, these substances at once dissolved, showing that the solution was probably due to cyanamidogen iodide, and I again presume the reaction to be in accordance with the formula:

$$2ICN + CaCN_2 = Ca(CN)_2 + I_2CN_2$$

Working of the Clancy Process.

I will now describe the general method of using the Clancy process on the working scale. The ore is crushed by stamps, rolls, ball mills or any other efficient form of preliminary grinding mills. The degree of fineness necessary for the process being about 100-mesh, this degree of fineness is probably most economically accomplished by the use of tube mills. The ore is crushed in the cyanide solution containing calcium cyanamide, sulphocyanide, and the halogen salts; it is therefore under the influence of straight cyanide treatment practically after leaving the rock-breakers until it reaches the agitation tank. In the agitation tank it meets with electrolysis, which acts upon the cyanide containing the additional chemicals in solution, forming powerful solvents for the precious metals, as already described. Before describing the treatment solution, the manner of dissolving the cyanamide should be known. Calcium cyanamide of commerce comes as a black powder, and is about from 58 to 65

percent soluble in water. It is necessary, therefore, to dissolve the cyanamide in a separate tank and filter from its insoluble residue. A small air-agitating tank is admirably suited for this purpose; at the same time it will act as a cyanamide storage tank. The cyanamide solution may be made as highly saturated as desired, and the calculated quantity drawn off when required and added to the cyanogen-bearing solution. The treatment solution is made up to 2,000 pounds of water containing 1 pound of cyanide, 2 pounds of alkaline sulphocyanide, 2 pounds of calcium cyanamide and ½ pound alkaline iodine. If using crushing rolls after the rock breakers, the product leaving the rolls at about 12-mesh is fed into the tube mill and converted into a pulp by feeding the mill with the treatment solution and ore in the proportion of one part of ore to one part of solution. The discharged pulp, after separation of the oversize, is transferred to the agitation tank to undergo electrical treatment. If it is thought necessary to remove the sulphides before, after or during the treatment, the following method presents an ideal scheme: When solution containing finely divided ore in suspension is contained in the well-known cone-shaped tank and agitated in the proportion of two of solution to one of ore, or in the proportion of three of solution to one of ore, if the agitation is stopped for a few minutes, the finely divided sulphide particles settle to the bottom of the cone, and by simply opening the discharge valve at the cone apex, the sulphide may be completely drawn off, together with a small proportion of the non-sulphide pulp. This sulphide product may be run over blankets or similar contrivances and the finely divided concentrate collected, the excess of pulp solution being returned to the agitation tank for treatment. Here is the means of eliminating the use of concentrating tables and obtaining a product of very high value in a very small bulk. Again, the pulp being in a very finely divided state, the pyrite or sulphide portion is not accompanied by quartz or gangue; therefore a clean high-grade concentrate is obtained, a result not capable of accomplishment by the use of concentration tables without the employment of a large quantity of solution with its attendant expenses.

The pulp now in the agitating tank carries the correct alkalinity, this being previously established in the tube mill by adding lime

so as to obtain from 0.1 to 0.2 pound "protective" alkalinity per ton of solution.

The conductivity of the pulp is adjusted by adding common salt until the required voltage is obtained; 20 pounds of salt per ton of solution, as already stated, will invariably decrease the resistance of the pulp so that the voltmeter will register about from 5 to 6 volts. In the majority of cases a current of about 50 amperes per ton of ore under treatment per day is adequate. It will be easily seen that the expense for electrical energy is not by any means prohibitive. With iron oxide electrodes it is possible to use a current density considerably over 50 amperes per square foot of anode surface, so that one electrode 3 feet in length by 3 inches in diameter will be sufficient for the treatment of from 3 to 4 tons of ore per day; in other words, approximately 30 of these iron oxide electrodes would be required for the treatment of 100 tons of ore per day. If the treatment tank is constructed of iron, the tank itself may be used as the cathode. This arrangement would, of course, decrease considerably the cost of installation. The electric generator is the chief item of cost. A low voltage generator, say, a 10-volt machine capable of giving the necessary amperage, can be obtained at any of the electrical supply houses. It is obvious, therefore, that the process may be applied to any existing fine-grinding plant provided with agitating tanks; all that is necessary is simply to introduce the electrodes into the circulating ore pulp containing the necessary chemicals, and switch on the current. It is essential in every case to maintain the alkalinity, *i. e.*, protective alkalinity, at about 0.1 pound alkali per ton of solution, so as to allow of the formation of cyanogen iodide and cyanamidogen iodide. About eight hours' treatment under electrolysis is usually sufficient to obtain the necessary extraction.

Regeneration of the Cyanide.

After the eight hours' treatment with the current, the pulp solution is brought up to about 1 pound per ton of protective alkalinity by adding caustic soda, and the cyanide contents regenerated up to about 0.5 to 0.6 pound cyanide per ton of solution. The regeneration of the cyanide is then accomplished simply by giving the pulp about two hours' more current. It will be understood that the reason for adding the extra alkali

is that cyanide regeneration cannot take place in the presence of a halogen compound unless the solution containing sulphocyanides and cyanamide is made alkaline.

It will be seen that the whole value of the process depends upon the recovery of the halogen compound. While I have described in the examples a proportion of two parts of solution to one part of ore, a proportion of three parts of solution to one part of ore may be used with advantage; that is to say, by using three parts of solution to one part ore, a much smaller amount of alkaline halide may be used per ton of solution, thus giving the same ratio of halide salt per ton of ore as in the two of solution to one of ore pulp, and consequently a less proportion of soluble halide to be displaced by the water wash in the final slimes cake.

Costs.

In this necessarily comparatively brief or incomplete description of the process, the use of chemicals and currents have been described, but no mention of costs has been referred to. I will, therefore, take the following solution to represent the typical working solution: 2,000 pounds of water, containing 1 pound of cyanide, 2 pounds of sulphocyanide, 2 pounds of calcium cyanamide and ¼ pound alkaline iodide. This appears a formidable mixture when looked at cursorily, but on analysis it does not work out beyond the limits of economic treatment. For example:

1 pound of cyanide	18 cents
2 pounds of cyanamide	6 cents
2 pounds of alkaline sulphocyanide	12 cents
¼ pound of alkaline iodide	35 cents
Total	71 cents

This would not represent the total cost of one ton of solution, for, notwithstanding the effect of electrolysis, practically all the haliod salt or salts perviously added, together with the sulphocyanide, will be found unimpaired at the end of the operation, the cyanide and cyanamide alone suffering the necessary decomposition. It is clear, therefore, that no matter what the proportion of solution to ore, only the consumption of cyanide and cyanamide per ton of ore is to be taken into account. The amount of cyanide consumption on the ore in presence of cyana-

mide works out at about 1 pound of cyanide per ton of ore treated. This consumption of cyanide is regenerated at the expense of 3 cents for cyanamide and, at the very outside, 3 cents for current (figuring current at 1 cent per kilowatt hour), making a total cost of 6 cents per ton of ore.

Added to the above cost is the cost of the electrical energy necessary for the electrolysis of the ore pulp. The cost of electrical energy for this purpose works out at about 10 cents per ton of ore treated; this, added to the cost for cyanogen-bearing material and regeneration, would make a total of 16 cents per ton of ore. These figures would represent the total cost, provided that all the solutions were recovered without mechanical loss. From this it is evident that the recovery of the solutions for re-use is a matter of vital importance to this process. The mechanical recovery of the solutions is, therefore, entirely dependent upon the efficiency of the filter employed.

The Moore filter eminently fulfils the process for the recovery of the solution, inasmuch as it gives perfect uniformity of cake both in thickness and porosity, which means perfect resistance, and perfect resistance guarantees perfect displacement. In fact, the business combination of the Moore filter with the Clancy process was originally brought about not from any arbitrary or usual business considerations, but because I, after the most rigid examination of all existing filter processes, learned in my demonstrations that this type of filter was the only one that could be depended on to recover practically all of the solutions.

This filter process is too well known to describe minutely; suffice it to say that when the final step in the cycle of treatment is reached, that is, when the cake has been washed with barren solutions, the moisture (containing soluble salts) saturating the cake at this juncture may be completely water-washed by giving it the requisite amount of water for displacement. The necessary amount of water for displacement is readily seen without calculation by the diminution of the water level in the wash tank; further, this can be adjusted to a nicety at the will of the operator, obtaining results not capable of accomplishment by any other known filter. It has been necessary for me to mention the unique points of this filter so as to show how the solutions can be recovered with a minimum of mechanical loss and with a minimum of water wash. In a properly constructed Moore

filter, Type A, the loss of solution under proper manipulation should not exceed 10 percent of the total solution.

It should be understood that the above figures are based on the treatment of rebellious or refractory ores, and that they would in all probability be much reduced when dealing with non-rebellious ores.

DISCUSSION.

Dr. N. S. Keith: I doubt the practicability of this process, because its complexity makes it too costly, even if effective. One feature of the mechanical treatment suggested by Mr. Clancy, that of concentration by the conjunctive use of cones and blankets in place of tables operated by power, is old—very old—and very inefficient.

The "protective alkalinity" phrase has a very indefinite value as he uses it. In the art, "protective alkalinity" is that amount of alkalinity which neutralizes the acidity of the ore; or, in other words, decomposes the various acid salts which enter into the solvent from the ores. These salts are so varied in character and quantity that in general practice large excess of alkali is used.

But in this case there can be no free chlorine, bromine or iodine in the solvent, if alkaline or even neutral.

The cyanide, as heretofore, can be regenerated by electrolysis at a much lower voltage and without the formation of KCNO.

The use of chloride of sodium in the solvent will result, by the use of such high voltage and density of current, in separating chlorine therefrom, which in large part will escape into the air and leave NaOH to increase the, to him, undesirable alkalinity, which must in some way be eliminated or neutralized before the solvent can be used again. If the solvent containing NaCl or sodium salts be used continuously in constant progression, according to economic practice, it would soon be loaded with these salts.

During the process of electrolyzing the solvent, gold must be precipitated on the cathode, where it would be continuously brushed off by the scouring motion of the pulp, to be re-dissolved.

If zinc be used as a precipitant of gold from an approximately neutral solvent, zinc cyanide accumulates in the solvent and is likewise precipitated on the cathode, where it is brushed off.

[*A belated reply by Mr. Clancy is printed at the end of this volume.*]

A paper presented at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 7, 1911, President Wm. H. Walker in the Chair.

SOME OBSERVATIONS ON LABORATORY PRODUCTION OF ALUMINIUM.

By H. K. Richardson.

It has been the writer's privilege to make a number of runs on the production of aluminium in the laboratory. These have proved so interesting that it has been decided to publish the results. All the work was done by students during the regularly scheduled laboratory periods. These students were chemists and metallurgical, chemical and electrochemical engineers. A laboratory process to be successful in the hands of these men must be simple, for some had had little or no experience in handling electrical apparatus for real work.

From the start it has been our desire to approximate as closely as possible the conditions of practice. In this work the student is expected to consider himself as working a commercial process. In his final report he is required to hand in a detailed estimate of the cost of running the process, using the laboratory data. Our earliest attempts to make aluminium were made in an apparatus similar to that of Tucker,[1] but results were not satisfactory, for two reasons:

1. The yield was seldom over 30-40 grams for a three or four-hour run. This corresponds to an ampere-hour efficiency of 20-25 percent.

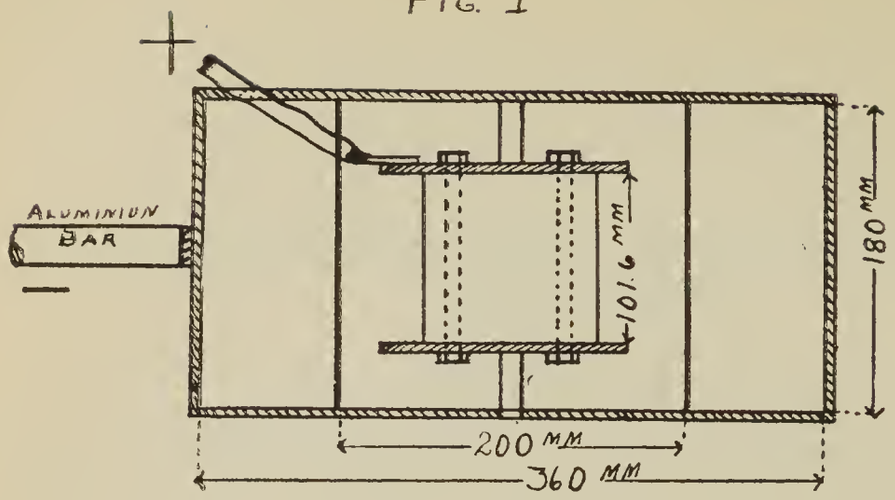
2. The apparatus and method of working are not comparable to practice.

Description of Furnace Used.

To more nearly approximate practice, a new cell was constructed according to the figures of a commercial cell given by Winteler.[2]

[1] Electrochemical & Metallurgical Industry, 7, 315.
[2] Borchers-Solomon; "Electric Furnaces," p. 210.

FIG. 1



PLAN

FIG 2

HEATING

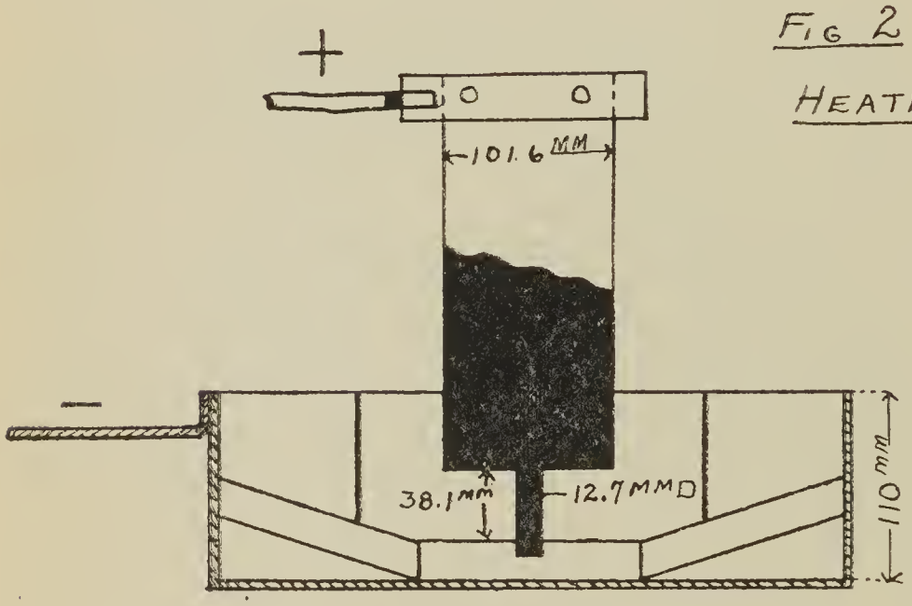
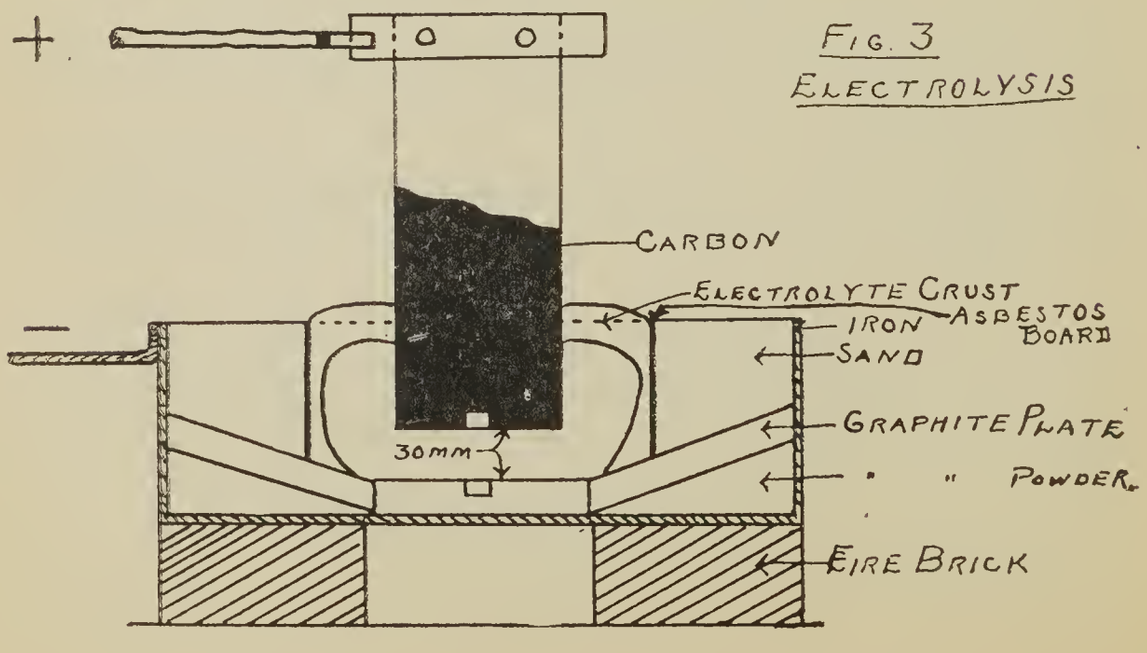


FIG. 3

ELECTROLYSIS



This cell, for 3,200 amperes, had the following inside measurements:

1,050 mm. (3 ft. 5⅜ inches) long.

550 mm. (1 ft. 9⅝ inches) wide

6,500 amp. per sq. meter (4.2 amp. per sq. in.).

As we had only 500 amperes available, we designed a cell of the following inside dimensions:

360 mm. (14.18 inches) long.

180 mm. (7.09 inches) wide.

110 mm. (4.33 inches) high.

The material used was ¼-inch (6.35 mm.) wrought iron plate, bolted to angle iron on all edges. The bottom was covered with an artificial graphite plate ⅞ inch (2.22 cm.) thick. A plan of this furnace is shown in Fig. 1, while vertical sections are shown by Figs. 2 and 3. It was our intention to use for electrodes three carbons 18 inches (45.7 cm.) long by 3 inches (7.62 cm.) diameter, thereby duplicating American practice. Before our cell was set up, the article by Neuman & Olsen[3] appeared, and it was decided to use two square electrodes 4 x 4 inches (10.16 x 10.16 cm.). However, we found two electrodes inconvenient to work with, so we finally made our runs with one electrode of above dimensions and 9 inches (22.9 cm.) long. This electrode was of common electrode carbon stock obtained from the National Carbon Company. The method of fusing the electrolyte used by Neuman & Olsen was employed. The heat was obtained by inserting a 2-inch (5.08 cm.) piece of ½-inch (1.27 cm.) carbon between the electrode and the bottom plate. See Fig. 2. This left 1½ inches (3.81 cm.) of the carbon exposed to do the melting. This length of carbon corresponds to 0.0125 ohms resistance. At the same time the furnace was shortened by placing asbestos board partition on each side 2 inches (5.08 cm.) from the electrode. The remainder of the space was filled with sand.

Fig. 2 illustrates this furnace set up ready to melt.

Fig. 3 illustrates this furnace set up with heating carbon removed and electrolysis taking place.

[3] Metallurgical and Chemical Engineering, 8, 185.

Instructions Issued for the Runs.

These instructions are the combined results of our experience and those of the various experimenters cited by Neuman & Olsen.[3]

The instructions are as follows:

1. Make 4 kg. of a mixture:

	Runs 1 and 2	Runs 4 and 5	Run 3
Alumina	20%	15%	
Natural cryolite	80%	85%	old charge

2. Melt up 3 kg. of charge at once. Add the remainder as the bath becomes diminished.

3. Remove the heating carbon as soon as the bath is thoroughly fluid.

4. Add alumina to bath every 30 minutes. Quantity to be calculated on assumption of 50 percent current efficiency.

5. Use anodic current density of 3 amperes per square centimeter.

6. If anode effect causes trouble, *i. e.*, current suddenly drops

   (1) Open and close circuit quickly

   (2) Add a charge of alumina

   (3) Tap electrode sharply

   (4) If none of the above are effective, add cryolite.

7. If voltage gradually rises at constant current, add, in order named, alumina, mixture, or cryolite, whichever brings the voltage down.

8. Keep crust broken on at least one side of electrode. Crushed coke around the electrode will tend to keep crust soft.

9. Take voltage and current readings every five minutes.

Results of Runs.

Fig. 4 shows the current readings in each of the 5 runs, 15-minute readings only being plotted.

Fig. 5 shows the voltage readings of each of the 5 runs, 15-minute readings only being plotted.

[3] *Loc. cit.*

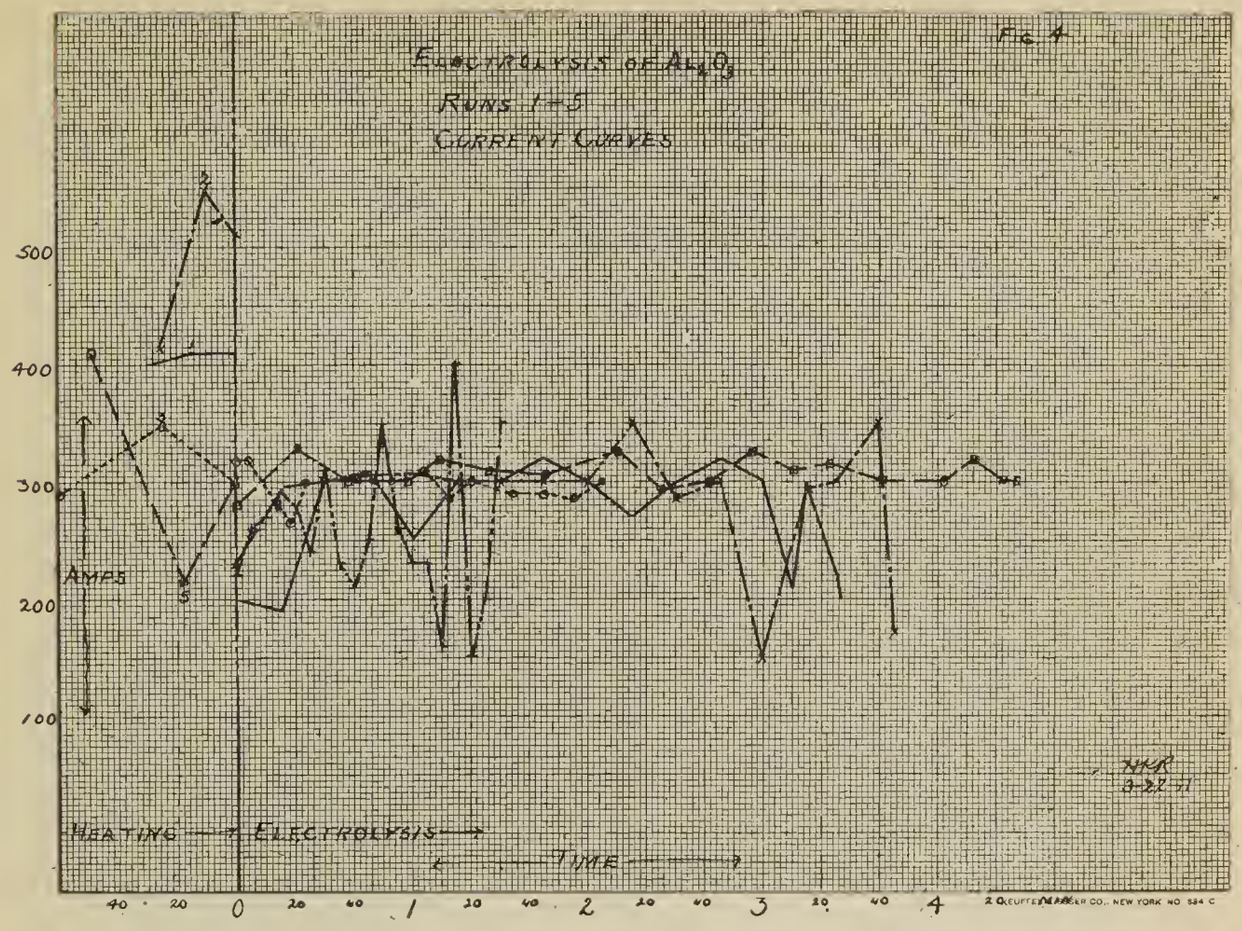
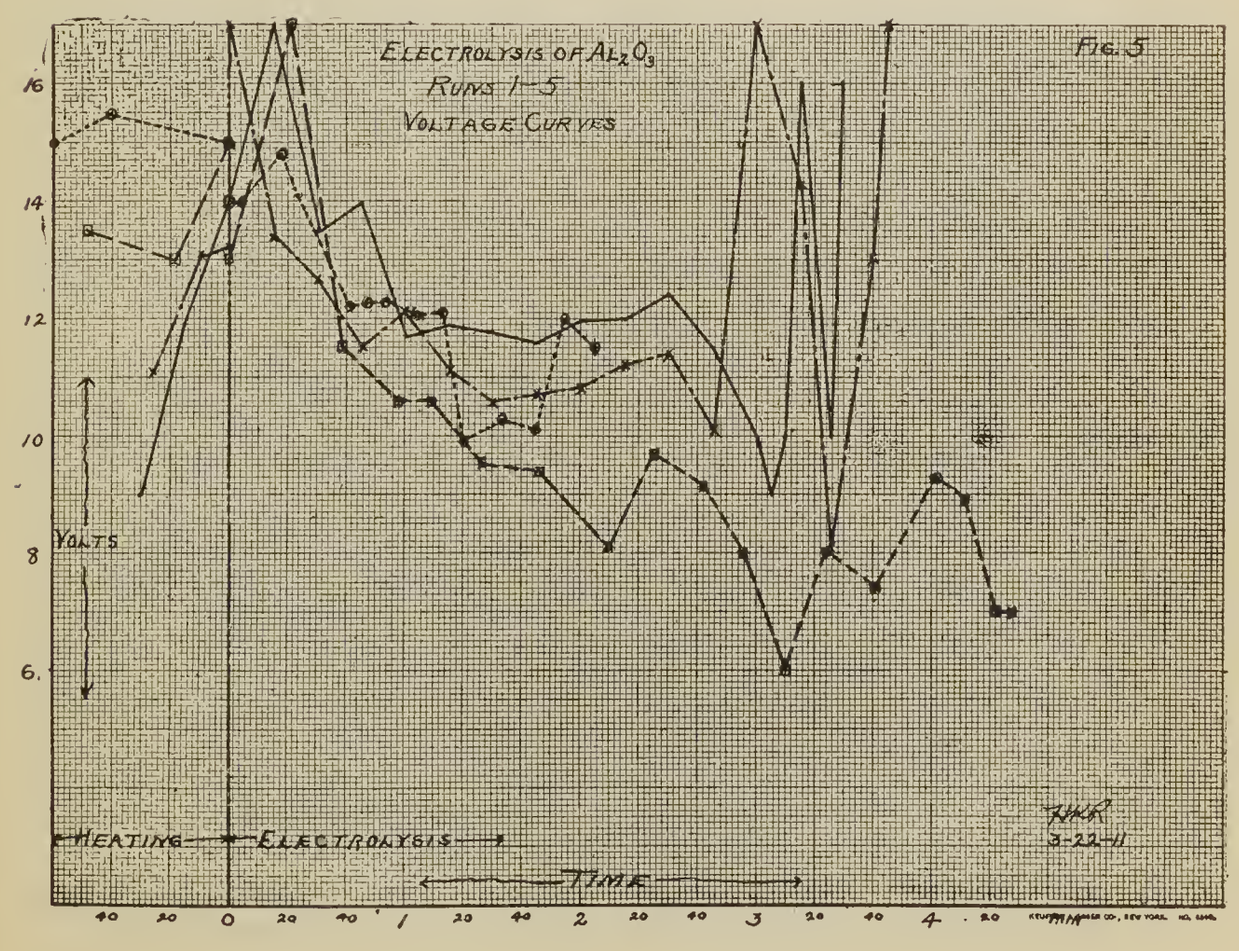


FIG. 4
ELECTROLYSIS OF Al_2O_3
RUNS 1–5
CURRENT CURVES
500
400
300
200
100
AMPS
HEATING
ELECTROLYSIS
TIME
40 20 0 20 40 1 20 40 2 20 40 3 20 40 4


ELECTROLYSIS OF Al_2O_3
RUNS 1–5
VOLTAGE CURVES
FIG. 5
16
14
12
10
8
6
VOLTS
HEATING
ELECTROLYSIS
TIME
40 20 0 20 40 1 20 40 2 20 40 3 20 40 4 20

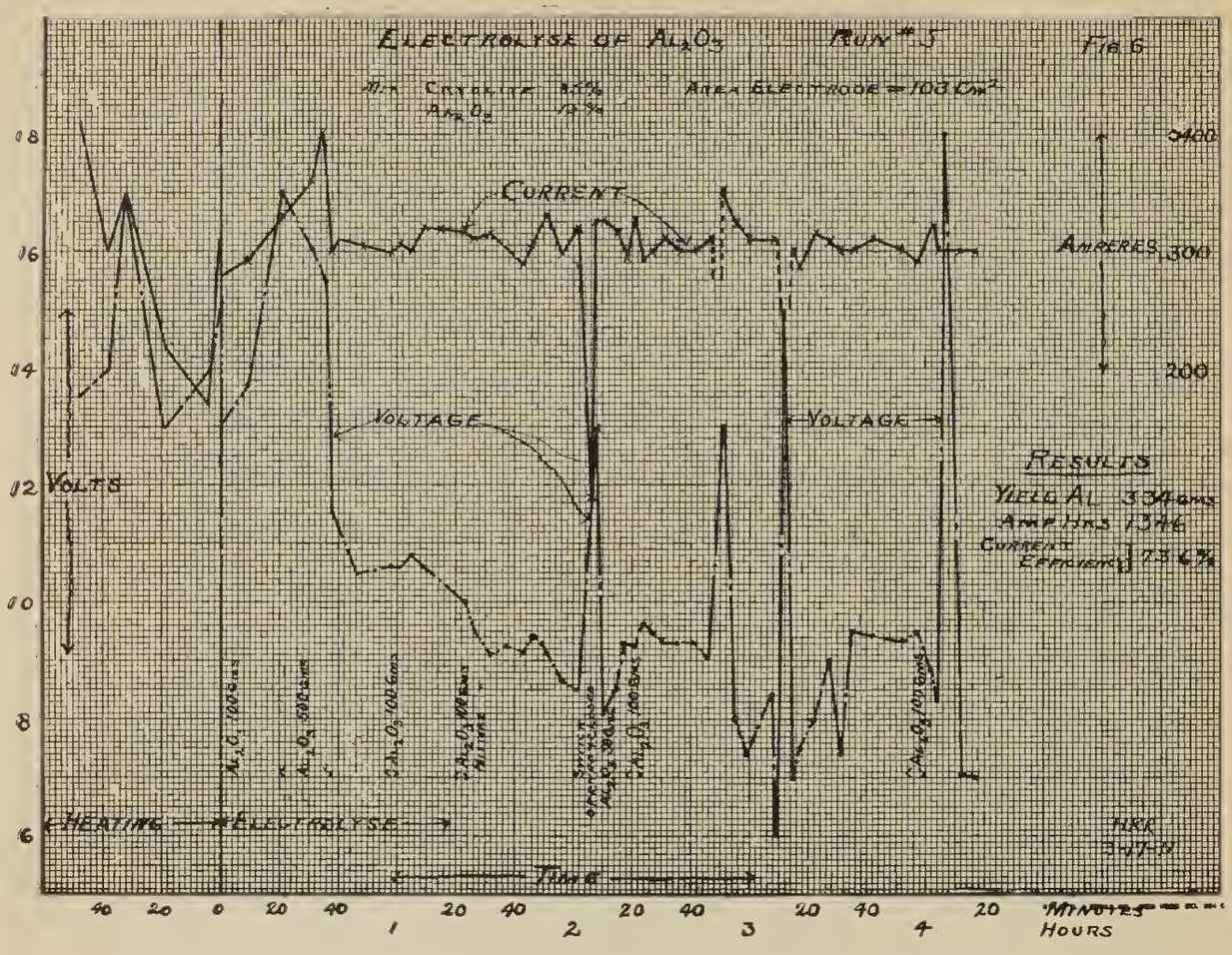


Fig. 6 gives the complete history of run No. 5. The foregoing instructions were more closely followed in this run than in any of the others, and it thus can be taken as a sample of the possibilities of the method.

The results of all five runs can be tabulated below.

Same apparatus used in every case.

Area of carbon anode = 103 sq. cm.

		Runs 1 & 2	Runs 4 and 5	Run 3
Mixture	Alumina	20%	15%	
	Cryolite	80%	85%	old charge

Run	Time of Electrolysis	Av. Volts	Av. Amps.	Amp. Hours	Yield Grams (*a*)	Efficiency (*b*)		Anode Current Density	
						Current	Energy	A/sq.cm.	A/sq.in.
						%	%		
1	3h. 27m.	12.5	269.4	992.4	168	50.3	11.2	2.62	16.8
2	3h. 45m.	12.5	284.6	1086.0	277	75.8	17.0	2.76	17.8
3	3h. 5m.	12.3	295.2	615.3	96	46.3	10.6	2.86	18.4
4	1h. 30m.	9.8	257.4	383.8	120	93.0	26.6	2.49	16.1
5	4h. 27m.	9.5	307.4	1346.0	334	73.6	21.7	2.98	19.2

(*a*) In most cases the aluminium was found in one or two large pieces; in two runs tappings were made However, in all runs small pieces were lost in the mix.

(*b*) Assume theoretical voltage 2.8.

No temperatures were taken, as a thermo-couple was not available at the time. The mix, however, was a bright cherry-red, temperature 900°-1000° C.

Tabulated Results of Various Writers on the Subject.

In this connection it is of interest to tabulate the results of previous experimenters. Data given other than writer's are taken from the article of Neuman & Olsen.

Experimenters	Type of Apparatus		Method of Heating	Charge			Volts	Amps.	Av. C. D. A/sq. cm	Ampere Efficiency percent
	Crucible	Anode		Al_2O_3 percent	Cryolite percent	Total kgms.				
Haber and Geipert	Carbon	Round Carbon	Arc	16.5	83.5	1.2	8 7	300 400	10.0	54.3 44.8 43.6
Thompson	Carbon	Round Carbon	Arc	20.0	80.0		13.5 11.8	180 390		38.0
Thompson	Graphite Box	Special Divided	Arc				10.7 8.8	500 1010	10.0 (Approx)	49
Richardson	Carbon	Round Carbon	Arc				17.0 7.0	148 450		22.6
Tucker	Carbon	Round Carbon	Arc	15	85		12 10	225		26.0 (Approx)
Neuman & Olsen	Iron Box carbon lined	Square Carbon	Resistance	10	90	12.0	13.6 8.0	150 280	1.17 1.48 1.70 2.15 2.68 4.15	31.8 45.5 49.8 49.6 60.8 53.0
Richardson & Students	Iron box carbon lined	Square Carbon	Resistance	20 15	80 85	4.0 4.0	17.0 8.1 17.0 5.8	150 320 160 400	2.62 2.76 2.49 2.98	50.3 75.8 93.0 73.6

Only the range of voltage and current is given, no attempt being made to keep the different experiments of each writer separated.

Observations.

1. A satisfactory laboratory run can be made upon aluminium, following instructions as given. The best results are to be expected under the following conditions:

Mix: 85 percent natural cryolite; 15 percent alumina.

Current Density: Approximately 3 amperes per sq. cm. of anode surface.

2. The anode effect appears to consist of two kinds:

(a) Gaseous envelope which opens the circuit. This can be remedied by opening and closing the circuit or tapping the electrode.

(b) Non-wetting of the electrode, thereby causing numerous small arcs to form from electrode to electrolyte. This causes the voltage necessary to be increased, and appears to be remedied by addition of alumina or cryolite, although it is present in some degree during the entire run.

3. In the hands of students, using the apparatus as above designed, and following the instructions as closely as students usually do, we should expect to obtain an ampere efficiency of about 60 to 70 percent.

Electrochemical Engineering Laboratory,
Pennsylvania State College, State College, Pa.,
March 22, 1911.

DISCUSSION.

Prof. J. W. Richards: I am exceedingly interested in this paper. I wish to comment on the note on page 164, in which Mr. Richardson assumes the theoretical voltage of decomposition 2.8. I think he has forgotten to take into account the return which you get from the oxidation of the carbon. The assumed theoretically required voltage to break up alumina is 2.8, but only about 2.25 is really required. I have measured that voltage in several ways myself, in practice, and find that the voltage absorbed in doing chemical work varies between 2.2 and 2.3 volts. That would make the energy efficiency less than you have it, because you credit it with 2.8 volts utilized, instead of 2.25, so that the energy efficiencies in your experiments are less than 26 per cent, at the best. That agrees substantially with the energy efficiencies in practice; so that if you consider the energy

efficiency in practice is about 25 percent, then 25 percent of the energy of the current is used for doing the actual chemical work, and 75 percent for keeping the bath up to normal operating temperature. This points very directly to the value of effort to reduce the conduction and radiation losses from the pots so as to keep them at the proper temperature, with *less* than 3 times the energy used up in chemical work.

Mr. Richardson assures me that the obtaining of 93 percent ampere-efficiency was a reliable determination. I do not doubt, but that by working at low temperature, at which the re-solution of the aluminium is small, nearly 100 percent efficiency can be obtained, but in actual practice the efficiency runs between 75 and 80 percent, showing 20 to 25 percent of the aluminium to have been re-dissolved. I believe that by a proper study the efficiency might well be brought up towards 90 percent in actual practice.

Mr. A. H. Cowles: Might it not really be 100 percent in actual practice, and thus conform to Faraday's Law? Dr. Richards mentions the re-dissolving of aluminium by the bath. If there is a re-dissolving there must be an electrolytic or rather galvanic action in connection with the re-dissolving, which is due to the attacking of the aluminium by the double fluoride bath, which is also in contact with the carbon walls of the pot, thus permitting local action and causing the re-dissolving of the aluminium, by the bath, as a fluoride. Now if the walls of the pot are made so that they do not form a couple with the molten aluminium at the bottom of the bath, we should have no re-dissolving, and I cannot see why the output should not come up to 100 percent, to correspond with Faraday's Law. As it is, the process, wherever employed the world over, is below 100 percent efficiency, and is thereby apparently contrary to the laws of electrolysis.

Prof. Richards: I think every fused salt tends to dissolve the metal which is contained in it as its base. If you electrolyze fused lead chloride at very near its melting point, you can get 100 percent ampere-efficiency. As you raise the temperature above the melting point, you get less efficiency, because of the solvent action of the lead chloride on the lead itself, until you reach the

boiling point, where you get zero efficiency. With caustic soda we find that within 30 degrees of the melting point, the yield is satisfactory. If you worked within 5 degrees, you get over 90 percent efficiency. If you work with the alumina bath close to its melting point, you get nearly 100 percent efficiency. There is a special reason why you cannot attain the 100 percent efficiency in practice. The specific gravity of aluminium cold is lower than that of the bath material, but when they are melted, at the high temperature of about 900 degrees, the aluminium is heavier than the bath material, and sinks below it. If, however, you get the bath cooled until it is near to its melting point, it becomes heavier than the aluminium, and the latter floats up to the top. You have to maintain such a temperature that the aluminium will not float up in the bath. At that temperature, the lowest you can practically run, you lose 25 percent of the metal, not by a voltaic couple being formed, but by the direct solvent action of the bath upon the metal itself.

Mr. Cowles: In the case of the electrolytic production of sodium we do get low ampere efficiency; the metallic sodium does float on the bath, and such flotation and oxidization would largely account for the low efficiency. But in the case of aluminium this metal stays at the bottom. Aluminium as a metal, without change to a fluoride, is insoluble in a double fluoride bath; it cannot dissolve without liberating an equivalent of sodium. Sodium is soluble in per-salts of sodium, forming normal salts. Peroxides of sodium form whenever oxygen reaches heated sodium.

As long as you have alumina and a double fluoride of aluminium and sodium forming a liquid bath, I cannot see why that bath is not like an aqueous solution of an electrolyte. The fluoride salts being the electrolyte and the Al_2O_3 being analogous to H_2O, a current passing through it should produce its equivalent of aluminium. I can see that when you use a carbon bottom and wall for your crucible, or have broken carbon in the bath, where the carbon is in contact with the aluminium you have a local couple, resulting in the passage of the aluminium into the bath and the freeing of an equivalent of sodium. Dr. Richards and I have had discussions on this point at times in the past, and have an

honest difference of opinion, and I would be glad to hear some other members take part in the discussion.

PROF. S. A. TUCKER: I have made many experiments in electrolysis with fused salts, and agree with Prof. Richards. The instance he mentions, the electrolysis of sodium hydrate, is a striking one. I repeated these experiments many times, and if the temperature as measured by a thermo-couple is much above the fusing point of the bath, you get no metal. As it falls to within ten or twelve degrees above that point the metal is seen to collect at the cathode, and you are able to recover it. I attribute the fact that you get no metal at high temperatures to the solubility of the metal in the bath. The same thing probably applies to aluminium.

My laboratory processes do not work as well as those described by Dr. Richardson, because they are carried on at a higher temperature. The reason I carry them on in this way is to shorten the process, which must be conducted inside of an hour, a longer time being impracticable with a large number of students.

PRESIDENT W. H. WALKER: What happens in the electrolysis of caustic soda, if you keep the bath at a high temperature?

PROF. TUCKER: You get no sodium.

PRESIDENT WALKER: What is the outcome if you keep on indefinitely?

MR. F. A. LIDBURY: In that case you simply get diffusion of the dissolved metallic sodium from the cathode to the anode, where it re-oxidizes.

PROF. RICHARDS: You can send a current of 900 or 1000 amperes through a pot as large as a silk hat, and the metal is carried back from the cathode to the anode as fast as the current separates it, and the bath lies "dead."

MR. LIDBURY: Is there any experimental evidence as to the solubility of aluminium in the molten bath? In the case of sodium there is, and I believe that Prof. Bancroft has shown good reasons for supposing the existence of sub-salts of aluminium. Has there been any experimental work published which tends to show the solubility of aluminium?

PROF. RICHARDS: I have a statement in my paper later on in the program, to the effect that all metals are soluble in their normal salts in a fused state.

MR. CARL HERING: If aluminum is dissolved in cryolite, where does the oxygen come from?

PROF. RICHARDS: It is a simple solution of the metal itself in the salt.

MR. LIDBURY: In reference to Prof. Richards' former remark, I would respectfully suggest that his statement does not constitute experimental evidence.

PROF. RICHARDS: There exists a good deal of experimental evidence on that point, but I would not wish to say that it covers all possible cases. But there is experimental evidence in many cases of the solubility of metals in their normal salts.

MR. LIDBURY: With reference to aluminium specifically?

PROF. RICHARDS: I have not the direct proof; but we know a number of facts which seem to indicate its solubility, of which, however, we do not have the direct experimental proof. Considerable discussion of this particular point may be found in Lorenz's "Elektrolyse der geschmolzener Salze," Volume II.

A paper presented at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 7, 1911, President Wm. H. Walker in the Chair.

AN ELECTROLYTIC FURNACE METHOD FOR PRODUCING METALS.*

By John Woods Beckman.

An electrolyte is generally understood to be a liquid which will conduct electricity, and the substances dissolved in this liquid are dissociated into two so-called ions. This was Arrehnius's theory, and has been applied ever since to water solutions. I believe though that O. Lehman and Lorenz and his co-workers are to be credited with having shown that the laws governing the water solution electrolyte are equally applicable to the molten electrolyte, and to substances dissolved in the same.

The above mentioned investigators have found and proved beyond a doubt that the substances dissolved in the molten electrolyte are ionised and that the Arrhenius dissociation theory applies thereto; also that the laws governing the dissociation, the movement of the ions, and the speed of their movements, can be determined the same in molten as in water electrolytes. Lorenz in his classic "Die Electrolyse geschmolzener Salze" has added through his painstaking work enormously to the knowledge of the fused electrolyte, the electrolyte of the future.

Up to the present time the industry which is making use of the molten electrolyte to the largest extent is the aluminum industry. The ionic theory has long been applied to the reduction of aluminum from its oxide, in the present well-known manner. Lorenz in the above-mentioned work publishes a very careful study made of the electrolytic deposition of aluminum from a molten electrolyte, and convincingly proves that it is an ionic reaction. His idea is confirmed by all who have studied the reaction and phenomena connected with the manufacture of aluminum, these

*This paper is what might be termed "preliminary." I hope at a later meeting to be able to give some details which, in the present experimental stage of the process, would not now be advisable to offer.

phenomena are identical with those met with in plating copper from a copper-sulphate solution.

I once had occasion to do a considerable amount of work in connection with the manufacture of aluminum, and then appreciated the simpleness of the procedure. It should be possible to produce all metals in a similar manner from their oxides; but what electrolyte is to be used?

In the aluminum industry cryolite is used as a bath material; a mineral mined at considerable expense, and together with that of the other ingredients used in the electrolyte, its cost is considerable. The fusing point of this electrolyte is low, and it is on this account suitable for producing metals of low melting points.

As a general law it can be considered that the electrolyte, fused or aqueous, from which a metal is to be produced should be a solution containing in some form the desired metal. Cryolite, containing mainly the metals sodium and aluminum, is on this account not suitable as an electrolyte for the production of any other metal than aluminum.

When most salts are heated to their melting point they dissociate, and this is especially the case with the salts of metals not belonging to the alkaline or the alkaline-earth metals. There are, however, exceptions among the heavy metal salts such as fuse but do not dissociate, and among these are the fluorides. Gin in his excellent monograph published in late issues of the Transactions of this Society, has outlined methods using the double fluorides of various rare metals, and using these as fused electrolytes out of which to produce the desired metals. But these fluorides have to be produced artificially, and although the process seems perfectly feasible, the cost seems to be prohibitive to using these electrolytes commercially.

A comparatively little known group of salts are those, occasionally occurring in nature, composed of equivalent amounts of calcium oxide and the oxide of any metal less positive than calcium. These salts occur occasionally in nature comparatively pure, as is the case with Scheelite, and can very readily be produced by heating the oxides together in any suitable manner.

It is evident that there is a great number of these salts possible, and the characteristic feature of them is, that they all fuse at

about and over 1000° C., the temperature varying according to the metal oxide which calcium-oxide is combined with. The boiling point of these salts is very high; I have heated some to 2200° C., and the molten bath has been perfectly quiet, without any appreciable signs of the ingredients boiling off. The valuable feature of these salts, that I have availed myself of, is that when in a molten condition they carry the current very readily, and are very suitable as molten electrolytes for the production of a great number of metals. On a small scale I have produced a number of metals using the corresponding salt as an electrolyte. Manganese, iron, chromium and a 50 percent alloy of vanadium are the metals that I have produced so far. In the case of the alloy, it is interesting to note that it was produced as well out of the sulphide as out of the oxide. Crude ore was used, giving not a pure metal, but one containing some impurities such as silicon, unobjectionable as far as the steel trade goes.

The following gives in brief the procedure in manufacturing a metal by means of a fused electrolyte composed in the manner mentioned above. Take for example iron. Equivalent amounts of Fe_2O_3 and CaO are mixed together and heated in any suitable manner. The salt $CaO.Fe_2O_3$ is formed and fused in a receptacle fitted for electrolytic purposes. Oxide of iron is introduced into this fused bath, and this molten solution is electrolysed, iron being deposited on the cathode and a lively oxygen development taking place on the anode.

If the electrolyte itself is submitted to the direct current, no noticeable reaction takes place, but the moment iron oxide is added the electrolysis starts, and by adding from time to time more oxide it can be carried on continuously.

The actual intermolecular phenomena that do take place when electrolysis goes on are hard to define, there may be a continuous rearrangement of the salt structure, the iron oxide in the salt becomes detached, and another molecule of iron oxide takes its place, while the former is ionised, and gives off its electrical charges depositing iron and oxygen.

This method of producing metals is protected by patents in U. S. A. (U. S. Patent No. 973,336) and in other countries.

The practical features of this method are: First, cost of electrolyte practically negligible, as it is composed of calcium oxide

and the metal oxide of the desired metal; second, a great quantity of metal can be produced out of the same electrolyte; third, in case the electrolyte becomes fouled, the loss in discarding the electrolyte is practically negligible; fourth, the flexibility of the process, making it possible to produce a great number of metals and their alloys such as iron, manganese, chromium, zinc, tin, titanium, vanadium, tungsten, tantalum, molybdenum, nickel, cobalt, lead and a number of others more or less rare.

In the following I am giving a list of amount of metal deposited per ampere-hour, considering only ideal conditions, and it is worth noticing, that aluminum has the minimum amount of metal deposited per ampere-hour, and is the only metal as yet that is produced commercially out of a fused electrolyte. Its use as a reducing agent for the production of many of the rare metals is well known.

Metal	Oxide	Gram per amp. hour.
Aluminum	Al_2O_3	0.3377
Lead	PbO	3.868
Chromium	Cr_2O_3	0.655
Iron	Fe_2O_3	0.696
Manganese	MnO	1.027
Nickel	Ni_2O_3	0.732
Zinc	ZnO	1.220
Titanium	TiO_2	0.445
Vanadium	V_2O_3	0.64

This process opens up a field which has heretofore been very little studied, and offers I believe a solution to many baffling electro-metallurgical problems.

I have here a few samples of metals which I have produced, made on a small scale in a graphite crucible. The principle of electrolyzing salts in a similar manner for the production of metals is well known, and the possibility of doing this is shown in a most striking manner in the production of aluminium by the Hall process. From the appearance of these metals it will be seen that the electrolysis has taken place at a temperature where the metals produced have been molten; anyone who is familiar with the nature of these metals—Cr, V, Mn,—will not be surprised to learn, deposited as they have been in a molten condition in contact with graphite, that they contain carbon.

An arrangement is easily conceivable in which these electrolyses could proceed without carbon present as cathode, and

under such circumstances the metals would be deposited free from carbon. In connection with this preliminary paper, I am not yet able to show any results of electrolysis carried on under such conditions.

As to the fusing points of these salts used in electrolysis, it is apparent that I am dealing with the mono-calcium salts. The temperature given as their fusing temperatures is based on actual observations, the details of which I have not at hand, and on data found in the literature. My recollection is that calcium manganite fused lowest of all, at about 960° C., while calcium aluminate fused close at 1400° C.

There is an interesting point in connection with these salts which seems to be worth scientific investigation. Supposing calcium aluminate to be produced, this consists of CaO fusing at about 3,000° C., and alumina fusing according to Mr. Saunders at 2,100° C. These two oxides are brought together and intimately mixed, and after being heated to about 1,100° C., there is no physical means of separating the two oxides; nor can the strongest microscope detect these constituents. A new compound is the result, and the reaction has taken place practically instantaneously, between two solids, forming a third substance which does not fuse except at a considerably higher temperature than the reaction or combining temperature, and at a much lower temperature than that of either of the contained oxides.

These phenomena could be classed under physical chemistry, and would be an interesting research to be taken up in detail in some college or university laboratory.

Niagara Falls, Canada.
March, 1911.

DISCUSSION.

MR. C. A. HANSEN: Is there any assurance that the metals Mr. Beckman is passing around are the results of electrolytic action? As I understand his paper, he passed direct current through various oxides or mixtures of oxides contained in graphite crucibles. In all cases mentioned the temperatures were such that direct reduction by carbon was entirely possible.

MR. J. W. BECKMAN: I can answer only by saying that it is a well-known fact that metals can be produced in this manner from fused salts. Electrochemical literature is full of it; the production of metals out of their fused salts is carried on extensively on a large scale all over the world. There is no doubt that aluminium is produced by electrolysis of a fused salt. I have not had a chance to make qualitative experiments, which would be the only way to prove conclusively that electrolysis takes place. I have noticed during my experiments an active development of gas at the anode which, even though I have not been able to collect and test the gas given off, cannot be anything but oxygen, indicating electrolysis.

MR. W. F. BLEECKER: I am interested in Mr. Beckman's statement that he has reduced metallic vanadium. I should like to ask him, if it is a fair question, what the electrolyte was, what the current conditions were, how much metallic vanadium was recovered, in what form, and what the method of reduction was. I think it is a well-known fact that up to the present time the production of pure metallic vanadium has been impossible, and if Mr. Beckman has a method of producing metallic vanadium it would indeed be a very interesting thing to get hold of some of the pure metal.

MR. BECKMAN: I will have to refer you to my paper, page 174, lines 9 to 15. I hope at a later meeting to be able to give some details which, in the present experimental stage of the process, would not now be advisable to offer.

MR. BLEECKER: I should like to ask how Mr. Beckman determines the electrolytic amperage for the deposit of the gram of vanadium, as stated in the table appended to his paper?

MR. BECKMAN: Mr. Bleecker has misunderstood the table appended to my paper. I do not give the electrolytic amperage necessary to produce one gram of metal, but I give the amount of metal produced per ampere-hour under ideal conditions. The determination of these quantities is very simple indeed, it is only a question of applying Faraday's law. From this table it is a very simple matter to deduce the number of ampere-hours necessary to produce one gram of vanadium or any other metal.

PROF. S. A. TUCKER: I am very much interested in this sub-

ject. Dr. Beckman carried on some of the work under my observation at Columbia. I have also seen experiments like this carried on before. It is very similar to the electrolytic process of making aluminium which we have tried on a small scale, such as I pointed out a short time ago in connection with the difficulties of making aluminium; there you have a variable current condition, giving arcing effect.

In the presence of an arc of 200 or 250 amperes, I am inclined to think there would be ordinary carbon reduction taking place quite as rapidly as electrolytic action, if not more rapidly, and it seems to me nothing in this or any similar process shows that it is an electrolytic action. I asked Dr. Beckman to point out to me why he thought it a purely electrolytic process and his answer to that was not clear. Mr. Hansen raised the same point, and I do not think there has been anything done to show it is electrolytic action rather than carbon reduction.

MR. BECKMAN: The heat of formation of alumina is exceedingly high, and I do not think Prof. Tucker would object to calling the present way of producing aluminium an electrolytic process. A very large ingot of aluminium, broken through and wetted, will show the presence of carbon; acetylene will be given off which would, according to Mr. Tucker's ideas, be proof that the process is not electrolytic. There are a number of citations in literature where a similar electrolysis has been carried out, not only with metals with lower heat of formation than aluminium, but with metals such as sodium, potassium, etc., forming pure metal by electrolysis in a fused bath.

PRESIDENT W. H. WALKER: Would it throw light on the subject to perform the same experiment with alternating current at high frequency?

PROF. J. W. RICHARDS: Light would be thrown on it if the same mixtures were placed in graphite crucibles and kept at the same temperature by external means, to see if you then get the same results.

MR. BECKMAN: You must have the temperature high, 1,400° or 1,500° C.

PROF. RICHARDS: The steel crucible is heated to 1,600°.

MR. BECKMAN: I made an experiment in which I tried to electrolyze the simple salt, without any result at all, but as soon as I put oxide in and electrolyzed I got metal out; which might partly answer the question.

MR. L. E. SAUNDERS: If Mr. Beckman has produced metallic aluminium from a compound of alumina and lime, it would be pretty good experimental evidence that it was electrolytic action rather than carbon reduction, because the production of metallic aluminium by carbon reduction is exceedingly difficult.

MR. BECKMAN: The production of aluminium in this manner is practically out of the question, because the specific gravity of the metal is too low and the aluminium would float to the surface and burn.

MR. BLEECKER *(Communicated)*: This process is very suggestive and it is certain that modifications of the idea will in the future have great commercial application.

There are some theoretically objectionable features in the process as outlined, in dealing with the oxides or other compounds of such elements as vanadium, tungsten, molybdenum, titanium, uranium, etc. For example, vanadium under these conditions will appear as an anode product excepting that a small quantity may be reduced by the carbon of the electrodes or the furnace lining. Moreover, any impurity in the bath will result in its equivalent loss of vanadium. This is not only true of impurities in the material to be treated or the bath, for at the temperature of the bath the vanadium will vigorously attack any known furnace lining. The bath will, therefore, not only foul quickly, but it will carry so much vanadium that the loss in discarding it will not be negligible. These are merely practical suggestions based on experience, data relating to the various heats of formation not being now available. I predict that future theoretical research will fully explain and verify the phenomena I have noted.

I can readily imagine that the reduction of any acid-forming element will present difficulties not yet appreciated in this paper. Moreover, those who have attempted to deposit zinc from the various fused zincates will agree that there are profound secondary reactions as a result of which the problem is still unsolved.

Mr. Carl Hering *(Communicated):* Mr. Beckman's process looks quite interesting. I notice, however, that he says free oxygen is evolved at the anode. This means that the electrical energy required must be at least equal to the whole of the chemical energy represented by the combination of the metal and the oxygen, and this portion of the energy will appear as a counter-electromotive force. Calculations, I believe, will show that in the case of a cheap metal like iron the cost of this energy is more than the value of the iron. Hence the process in that form is not likely to be a commercial one for the cheap metals. When iron oxide is reduced by means of carbon, as for instance in the blast furnace, the net energy required for the reduction is only the difference between the energy of combustion of iron with oxygen and that of carbon with oxygen, as the oxygen is not set free as such; this difference is relatively small. If, therefore, it is possible in his process to use as an anode a material which would combine with this oxygen and thereby give off energy, the electrical energy required ought to be much less. Perhaps an anode of carbon, say in the form of coke, would do this. In the reduction of aluminium the anode oxygen, I understand, combines with the carbon of the anodes, and hence is not set free as such.

Concerning the electrolytic properties, it is in my opinion not to be recommended to make any typical distinction between fused compounds and such as may be liquid at ordinary temperatures; whether the fusing point of a compound happens to be above or below ordinary temperatures is a matter of chance and ought not to make any typical difference in its behavior as an electrolyte. Water, for instance, must be considered to be the fused oxide of hydrogen. A better distinction would seem to be to consider a true fused compound as different from a dissolved compound. But then it should be remembered, as Dr. Kahlenberg emphasized some years ago, that there are many other solvents than water.

The metallic fogs ("Schliere"), in the classic researches of Lorenz, seem to me to be analogous to the deposit of mercury on a vertical cathode. The mercury being a liquid, naturally flows down and collects on the bottom, thereby forming a short-circuit with the anode unless prevented from doing so.

MR. BECKMAN (*Communicated*): Mr. Bleecker's discussion has been read by me with great interest. I doubt his theoretical objections. "Vanadium under these conditions will appear as an anode product" is one statement made, and though Mr. Bleecker does not make it clear that he means an oxide of vanadium to be the anode product I take it for granted that such is the case. It is very probable that such would be the case if vanadium salts in water solution were electrolyzed, but to find any lower oxides deposited on the anode from electrolysis of a fused electrolyte is, I believe, not to be expected.

I think the other objections Mr. Bleecker offers are very proper, but that they are all of such a nature that it is only a question of continued experimentation to overcome them.

The electrolysis of fused salts is not always easy, and it is a question of carefully regulating voltages and current densities to be able to carry them out successfully. Mr. Bleecker's troubles in electrolyzing fused zincates may partly be due to such causes.

Regarding Mr. Hering's communicated discussion, I have never thought it likely that my process would be applicable to the cheaper metals, like iron. Of course in the case of iron, carbon anodes could be used for the oxygen to combine with and, for all metals that have not exceptional attraction for carbon, anodes of carbon could be used; but for the more rare metals like titanium, vanadium and others, which have a very great tendency to absorb carbon, it is preferable to use an anode material that does not contain carbon. The price of these rarer metals is so great that the use of such anodes is justifiable, especially as a carbon-free metal is of the greatest commercial value.

I believe that the first three lines in my paper cover the point Mr. Hering considers regarding electrolytes. My definition of an electrolyte distinctly stated "a liquid which will conduct electricity, and the substances dissolved in this liquid are dissociated into two so-called ions." This definition includes all kinds of electrolytes, whether liquid due to high temperature or not.

I doubt that Mr. Hering's suggested distinction would improve matters in regard to fused electrolytes and water-solution electrolytes.

A paper read at the meeting of the Chicago Section of the American Electrochemical Society, January 20, 1911. Called up for further Discussion at the Nineteenth General Meeting of the Society, in New York City, April 7, 1911, President Wm. H. Walker in the Chair.

ELECTROLYTIC REFINING AS A STEP IN THE PRODUCTION OF STEEL.

By Charles F. Burgess.

During the past five years a lengthy investigation has been carried on in the Chemical Engineering Laboratories of the University of Wisconsin dealing with electrolytic refining of iron and its use in the production of alloys. About three tons of iron has been refined and over one thousand alloys produced and tested.

While this experimental work has been on the "test tube" or laboratory scale, it is believed that some of the results indicate the feasibility of enlargement to a commercial scale, and a short discussion is submitted here bearing on the question, "can electrolytic iron be made an industrial product?"

Many old text-books on electrochemistry give descriptions of methods of depositing iron electrolytically, implying therefore that electrolytic iron is not a new product. The only use suggested, however, is for facing engraved plates used for printing. By following any of these earlier processes it is seen that only very thin layers of iron can be deposited, the coating tending to become dark, rough, and powdery. It is to overcome this limitation that the work at the University of Wisconsin was undertaken, and that this has been successful in a measure is indicated by the production of an iron cathode nearly two inches in thickness.

The manner in which electrolytic refining has revolutionized the copper industry is now an old story, and electrolysis has likewise become an industrial agent in the metallurgy of silver, gold and lead. Now that it has been found that iron can be refined electrolytically almost as easily as can copper, it is pertinent to inquire whether there is a field of usefulness for such iron. This depends upon whether electrolytic iron has superior qualities due to purity or physical condition, and whether it can be procured at low cost.

From the standpoint of purity it must compete with some notable metallurgical developments which have resulted in the product such as is being made by the American Rolling Mill Company in a basic open-hearth process. For this material a purity of 99.94 percent is claimed, and justifiably so, as some of our analyses show. The electric furnace is another factor which is contributing largely to the control of the composition and purity of iron alloys, and the striking possibilities which are offered in this developing field cannot be overlooked in advocating the development of an electrolytic iron process.

The chief source of commercially pure iron has been, and perhaps now is, the high grade Swedish and Norway iron, used largely as a base material for high-grade crucible steel. The analyses of this material usually indicate a high purity, though frequently and erroneously calculated by difference after determining carbon, sulphur, silicon, phosphorus and manganese. It is not uncommon to find oxides and slag to the extent of two percent in this material, and this impurity undoubtedly may have an influence on the resulting alloys made from it.

We have found that electrolytic iron can be produced with a purity as high as 99.97 percent and perhaps even better, using extraordinary precautions. This record has been made by using the best commercial grades of pure iron as anodes. A few hundredths of a percent of purity must be sacrificed in using anodes of mild steel or other less pure materials. Electrolytic refining offers a means of reducing or screening out most of the impurities commonly found in iron, and of producing a material not only of high purity but of great uniformity. Even though it may be shown eventually that electrolytic iron may not have a higher purity than that attainable by other methods, the uniformity of its composition should make it a valuable material as a means of eliminating many of the variables with which the crucible steel maker has to contend.

Using an electrolyte containing 40 grams of iron per liter in the form of ferrous sulphate together with 40 grams of ammonium chloride, it has been found possible to conduct a continuous refining operation for many months at a current density of 6 to 10 amperes per square foot of cathode surface, and at

a potential difference of about one volt. The current efficiency is very close to 100 percent, as it is in copper refining.

This leads to the calculation that one kilowatt hour will refine two pounds of iron; or a cost for power of ½ cent per pound is attainable. The cost for labor, solution maintenance, and fixed charges are estimated to be not greater than the power costs, making a cost of refining of about $20 per ton. Assuming the anode material to be mild steel costing $35 per ton, the cost of electrolytic iron would be in the neighborhood of $55. These approximate calculations indicate that this material might well compete on price with high-grade Swedish iron.

Among the properties of electrolytic iron which may give it some added usefulness is its content of hydrogen and the brittleness which results from this occluded gas. This hydrogen may be of some service in reducing oxides in a melt. The brittleness of the electrolytic iron before the hydrogen is driven off makes it easy to break it up into pieces suitable for introduction into the steel crucibles.

DISCUSSION.

(At Chicago, January 20, 1911.)

MR. F. T. SNYDER: I would like to ask Professor Burgess whether he ever used the molten condition in producing iron electrolytically.

PROF. C. F. BURGESS: Only to a very slight extent. We got no encouraging results.

MR. G. H. JONES: One point I consider very important is the cost of the current. Using it during the off months or at the off times of the day, the rate of the ordinary charge for the refinery will be almost one-half of the ordinary price, and that will make it very low indeed and ought to help out a great deal in this business.

PROF. H. N. MCCOY: At what times in the day, Mr. Jones?

MR. JONES: From four o'clock to eight o'clock in the afternoon during the months of December, January and February.

All the other months you can use it all the time, but not during those four months,—those are the off months.

Mr. C. E. Baker: I would like to ask Professor Burgess if he ever tried electrolyzing iron from chloride solutions.

Prof. Burgess: You cannot get deposits of iron from chloride solutions as satisfactorily as from sulphate solutions. However, it is simply a question of adjusting your electrolyte so you can build up a big deposit, and which will be cheaper. Other experimenters have reported satisfactory results from chloride solutions, but we have not succeeded in getting satisfactory results.

Mr. W. Bently: I would like to ask Professor Burgess if he has the electrodes in motion in depositing the iron; whether they are moving while the iron is being deposited or whether they are stationary in the solution.

Prof. Burgess: Everything is perfectly quiet in the tank. We have tried the effect of rapid circulation and slow, and find little if any change in it and, in fact, the tanks are left for several months without cleaning out, that is, without cleaning out the deposits at the bottom; but once a week the solution is circulated through a series of tanks, just circulating two or three times.

Mr. Bentley: The reason I asked that question is because I believe in certain plating work, by rotating the electrodes quite rapidly a deposit which is more uniform and which is smoother and freer from crystals or crystalline structure is obtained, and I was wondering whether it might not have some effect with iron.

Prof. Burgess: Of course, what we tried to do was to work out a process for doing this as economically as possible and if you figure the cathode investment in moving the electrode throughout your entire plant, it would be a very expensive proposition. We have tried to deposit iron tubes by rotating the cathode, but never got any better deposits than when having them quiet.

A paper read at the Meeting of the Chicago Section of the American Electrochemical Society, January 20, 1911. Called up for further Discussion at the Nineteenth General Meeting of the Society, in New York City, April 7, 1911, President Wm. H. Walker in the Chair.

THE RELIABILITY OF ELECTRIC FURNACES FOR COMMERCIAL WORK.

By Fred T. Snyder.

A few days ago a man who had been East attending the meetings of an association of engineers representing an industry that uses a large amount of high-grade steel, in various forms, was asked about the electric furnace paper on the program. He characterized it as "the usual optimistic hopes by the agent of an electric furnace inventor." While without the furnace inventors, and without the optimistic hopes that held them for ten years to the expenditure of time and energy and money that was all outgo and results deferred, there would be no commercial electric furnace work to-day to consider, it now seems as though the time had come to point out to those who are less closely in touch than ourselves that the electric furnace has grown beyond a question of this inventor or that inventor, has grown beyond a question of hopes to one of commercial use, and is now a matter of engineering and finance; today the electric furnace has achieved reliability.

But before the time goes by when particular arrangements of electric furnaces are called after their inventors, as such time has gone by for the open-hearth furnace and for the crucible furnace, it would seem proper that we should call by the name of its inventor that simplest of all electric steel furnaces, in which a single electrode above leads the current through an arc to the steel, and a metallic contact with the steel bath below leads the current back to the dynamo. Back in 1880, so far back that the paper describing it was read before the "Society of Telegraph Engineers," as then the only representatives of electrical engineering, William Siemens built and operated his furnace, in which the heat of the electric arc was used to melt steel. This little furnace was a practical furnace. It made good steel. A dupli-

cate of it, copied from the old drawings, will today work without difficulty, making its little batch of steel. It is especially notable that it is to this same William Siemens that the steel industry also owes its open-hearth furnace, second only in importance to the blast furnace itself. As the Siemens electric steel furnace was the first practical electric steel furnace, so now it bids fair to be also the furnace to be used in the greatest numbers. It is characteristic of the electric furnace that it is reliable in small units, and it is in this direction that the future is tending, towards the making of some steel castings by many of the grey-iron foundries, and the making of their own steel castings by many of the larger users. In these small installations, the simplicity and reliability of the Siemens electric steel furnace will be important. With proper engineering, this single-electrode type of steel furnace can be built reliably up to 500 kilowatts, a production of 250 tons of steel per month with continuous operation. In point of numbers, many more than a majority of commercial installations will be below this tonnage. A worthy use of this opportunity will be to emphasize the good to electrochemistry that has lived beyond the life of this man, by calling this type of electric furnace the Siemens furnace.

Broadly, reliability is commercial, the ability to make a profitable return on an investment. That the electric steel furnace is reliable in this way is emphasized by the growth of those plants in Europe that are making electric steel exclusively. And beyond steel making, the electric furnace has been commercially reliable so long in the aluminum industry that the general patents have run out. The commercial reliability of the electric furnace in the manufacture of carbide has for years been in evidence with each user of acetylene light. Less widely known, but commercially profitable, has been the electric furnace manufacture of carbon-bisulphide, of phosphorus, of graphite, of abrasives, of magnesium for flashlights, of ferro-alloys for steel refining, and in the last few years we have seen the reliability of electric furnace operations pledged in the investments of the millions of dollars that are going into the construction of huge electric furnace plants for the production of fertilizers. And it is the commercial reliability of these older electric furnace applications that is back of the reliability of the newer application of the

electric furnace to steel. In them was developed the demand for electrodes which justified the building of electrode factories that now are available for steel furnaces. In them was developed the special engineering ability to handle the large electric currents of furnace work. They had their part in the demand for electric current at lower and lower cost. It is these things that have given the Siemens electric steel furnace of thirty years ago—a technical curiosity then—its standing today as a reliable industrial tool.

Technically, reliability is a matter of apparatus and men and supplies. These react on one another. Experienced and skilled men can force poor supplies and indifferent apparatus to yield a commercial output. Apparatus that is inherently self-regulating will permit the use of such men as can be had at a permissible cost. Supplies that have a factor of safety in their constitution will carry the equipment through an overload. Involved in the question of commercial reliability is the element of time. Results must be prompt. To make electric steel in the United States means furnaces that are reliable, with American men and American supplies. In the rush of industry, reliability cannot afford the time hazard of importation. Europe developed the electric steel furnace industry first, just as it developed the dynamo first, the steam turbine first, the large gas engine first, steel making first. There the pressure of competition for opportunity, the abundance of trained technical men, and the low cost of capital, force enterprise. Safely we may look in America, with the electric steel furnace, for the same swift overtaking of achievement that has characterized those other technical developments. For this, reliable American electric furnace supplies are now available and tested. American electrodes can be had in sizes as large as furnace requirements call for. Refractories made in this country have been developed with an ability to stand up well under the higher temperature of the electric steel furnace. Campaigns with roofs of American brick have run into months, as against weeks for European practice. Skilled electric furnace men are scarce. The rapid installation of furnaces more than absorbs the few who have had an opportunity to become experienced with electric furnaces working in commercial operation. Trials with electric furnace men imported have not been wholly satisfactory.

The drive of the American steel plant does not seem to fit with the methodical nature of the foreign technician. This shortage of skilled furnace men at permissible costs has thrown more of the burden on the apparatus, has directed American electric steel furnace design toward inherent self-regulation, as we say electrically; toward reliability, as the investor looks at it; toward making it "fool proof," as the man on the job phrases it. Furnace detail that works very well in Europe, with the skilled help available there, has to be designed here to work with the help that can be had. This inherent reliability can now be carried to an extent that permits taking a steel melter from a crucible or open-hearth furnace and putting him on an electric steel furnace with the assurance that within a week he can be making salable steel regularly. This does not mean making an electrician of him. Actually he knows no more of electricity than he knew of the kinetic theory of gases in his open-hearth work, but he does know that when the watt-meter needle is in a certain position he has a supply of heat in his furnace, and high temperature heat at that, and heat that, hot as it may be, will not burn his steel.

But a reliable furnace and reliable supplies and reliable melters are not all that are concerned in the commercial reliability of electric steel. The steel produced is different from crucible steel. It is different from open-hearth steel. If it were not different, the electric furnace would not be used. It is true that under favorable conditions steel can be made cheaper with an electric furnace than in other ways, but the fundamental reason that is speeding electric furnace construction is that the steel is better. Being better means differing chemically, differing physically from the steels of the other furnaces, and this difference chemically and physically must be reckoned with in the subsequent processes the steel goes through. In the foundry the moulding must be done for this new material. It is freer from gases. It usually is hotter. The tendency is to lower the carbon for the same tensile strength, and this makes it set at a higher temperature. The improved elimination of phosphorus and sulphur tend in the same direction. In the forge and rolls, electric steel shows its additional strength and toughness. It must be handled from the point of view of its characteristics. It is a mistake to simply consider the electric steel furnace as a substitute for some other

kind of a melting furnace. Its introduction can be counted on to mean changes of method as far as the steel is followed in manufacturing processes, and unless this is clearly recognized there will be disappointment, and the reputation of the electric furnace for reliability will suffer.

From a still narrower technical point of view, reliability means freedom from actual breakdown, from the enforced necessity of change in construction and the consequent loss of time and productive capacity. As to this, electric furnace design is now on an engineering basis. Dependence on experiment is now a matter of volition on the part of the investor. It is no longer a necessity. As a piece of engineering apparatus, an electric furnace can now be more closely designed to meet narrow specified operating conditions than can an open-hearth furnace. In a recent instance, an electric furnace and a small open-hearth were installed side by side in a new steel casting shop. The open-hearth gave trouble, and has been replaced by a better design. The electric furnace, although not of most modern design, has operated without need of alteration. Those details in which an electric furnace differs from established open-hearth practice, the electrode holders, the electrical regulation, the contacts with the bath of steel, are now rugged and simple. Electrode holders are in evidence that operate with less than one hour's lost time in 100 heats. Recently I have had occasion to examine carefully in detail the condition of a plant using electric furnaces exclusively, that started operation on a commercial scale in the summer of 1907, which is quite aged as electric furnace design goes. It is proposed to double the size of the unit and increase the size of this plant fivefold, and this examination was made to determine from the condition of the plant and the operating history what changes in the original design could be made to advantage in the extensions. Incidentally, the examination disclosed a condition of continuing reliability that is worth recording. Substantially all of the original equipment was still in use. The plant, which is in the West, has been operated since its installation by Chinese labor under a white superintendent, and neither the superintendent nor the Chinamen knew more of electricity than is involved in the opening and closing of circuit breakers and the reading of ammeters and voltmeters. One of the power

transformers had been replaced, but it was learned after its removal that the trouble was an abraded spot on a terminal that could have been readily repaired on a Sunday at the plant. This particular plant, while not a steel plant, is of interest in showing on many of its operating records a heat development efficiency of over 90 percent. That is, of the heat equivalent of the energy delivered to the plant by the high potential electric wires, over 90 percent is transferred to the material under treatment.

It is to be expected that the success of this new and flexible tool of industry will lead to overenthusiasm and its application in wrong ways and in wrong places, and that its failure as a panacea for troubles it has properly nothing to do with will bring setbacks. But back of its present success is the cause of that success, the steadily lowering cost of electric current. Thirty years ago the furnace of Siemens worked as an apparatus. It was not until the cost of current dropped below the figure at which the electric furnace was commercially reliable in this country that its industrial application began and its engineering developed. This dropping of the cost of electricity is still going on, and as it goes on it brings a greater and greater motive force to bear on the installation of electric furnaces. At the same time, unfortunately for industry in general, but fortunately for the electric furnace, the cost of fuel for direct and gaseous heat is slowly but steadily rising.

Summed up more briefly, the facts that an investigator of electric furnace results may expect to find are:

1. That the electric furnace itself has passed from the field of experiment to that of engineering, but that the fields of manufacture using the electric furnace products are still experimental.

2. That the electric furnace is technically reliable and will operate continuously with the men and supplies that are available in this country. That the details are simple and rugged, and that the inherent regulating powers can be made such as to bring it well within the ability of usual plant labor.

3. That the electric furnace is commercially reliable. That when installed with the same business care and adaptation to conditions that should be used with other furnaces, it will earn a profit on the investment, and a profit that is larger than the normal manufacturing profit in proportion as the field is newer and more open.

DISCUSSION.

(At Chicago, January 20, 1911.)

MR. BREGOWSKY: I would like to ask in particular if there are any electric furnaces designed for brass.

MR. F. T. SNYDER: They have been used for the melting of copper quite extensively in commercial work, and the electric melting of brass has been carried on also, but I don't know of any furnace that is running regularly commercially melting brass, that is, as far as using a furnace built only for melting brass itself is concerned.

MR. BREGOWSKY: In melting copper is there much oxidation?

MR. SNYDER: Not in melting copper. They use a deoxidizer, just as they do in steel. Consequently they get a copper which is very much freer from oxidation than the ordinary copper refining furnace produces.

(At New York City, April 6, 1911.)

MR. F. A. J. FITZGERALD: We have observed that, in our particular field of work, ill-considered assertions about a particular process or apparatus frequently do it harm. This is sufficient basis for a criticism of Mr. Snyder's assertion that a certain plant "is of interest in showing on many of its operating records a heat development efficiency of over 90 percent. That is, of the heat equivalent of the energy delivered to the plant by the high-potential electric wires, over 90 percent is transferred to the material under treatment." Considering that the loss of energy in the transformers, which presumably are used in connection with the "high-potential wires," must amount to about 3 percent, there is left only 7 percent for the losses by radiation and the various other causes inevitably associated with work of this kind. It is not intended to deny the accuracy of Mr. Snyder's statement, but merely to point out that such an extraordinary observation should be at least substantiated with an account of the methods used in arriving at the result.

MR. SNYDER (*Communicated*): In the interests of conservatism, the actual efficiency was not stated quite as high as our measurements determined it. The plant in question is the electric

turpentine distillation plant designed and built by our company in 1907, and described by the writer in Vol. XIII of the Transactions of the American Electrochemical Society. When the question of designing the new and larger plant was taken up, a number of determinations were made on the old plant to determine the constants of design for use with the new plant. The figures varied somewhat with the different runs, but the following are typical:

Average load on high-tension side of transformer 36.8 kw.

Loss in transformer 1.1 kw.

Loss in leads and switches 0.6 kw.

Radiation loss 1.5 kw.

Absorbed by wood (by difference) 33.6 kw.

The transformer loss was determined by the usual method of short-circuiting the secondary and measuring the input with full-load current in the secondary. The local line loss was determined by the voltage drop to the retort terminals. The radiation loss was determined by holding the temperature constant within 1.7° C. for about eight hours on a can of charcoal and taking the wattmeter input. These figures correspond to an over-all efficiency of 91.2 percent.

The low radiation loss is due in part to the low maximum temperature, 190° C., but mostly to the design of the retort in the form of flat slabs, which are stacked together so that there is a radiation loss on the edges only. The figures above apply to one retort only. In the new plant, the input per retort will be 100 kw. and the radiation is calculated to take 3 kw.

A paper read before the Chicago Section of the American Electrochemical Society January 20, 1911; also called up for further discussion at the Nineteenth General Meeting of the Society, in New York City, April 8, 1911, President Wm. H. Walker in the Chair.

THE ELECTRIC FURNACE FOR THE MANUFACTURE OF IRON AND STEEL.

By James Lyman.

The recent development of the electric furnace for the manufacture of iron and steel registers a distinct advance in the art. We may expect its rapid introduction especially as a refining furnace.

It is therefore well at this first meeting of our new section to briefly consider the features of this new process of making iron and steel that are superior to the old processes. More and more the manufacture of iron and steel is becoming highly scientific. The analysis of the ore or the iron treated, and of the flux and fuel used, is made at the start, and from time to time afterwards until metal of the chemical characteristics desired is obtained. All losses of heat, material and labor are reduced to a minimum, and the maximum output of furnace is sought. Where the product is to be rolled or forged, the greatest care is used to produce the most dense and uniform grain of the metal.

Highly skilled chemists, mechanical and electrical engineers have wonderfully improved and increased the output of our iron and steel mills in recent years. They have probably developed the present processes to very nearly their limit of perfection. There are, however, certain inherent characteristics of these processes that prevent obtaining the very highest qualities of iron and steel. For instance, these processes depend upon various fuels as the source of heat, and during the treatment for the elimination of harmful ingredients, certain foreign impurities, such as nitrogen and oxidation products, enter the bath, injuring in a measure the desired qualities of the metal. Further, there is not always a perfect homogeneity and soundness of metal throughout the entire charge, and either the chemical analysis

of different charges or the physical properties of these charges, or both, may vary considerably.

Many metals, including iron and steel, are refined by melting them in contact with a slag composed of ingredients which will absorb their impurities. For the most effective action, the slag must be fluid only at the highest temperatures. The electric furnace is capable of creating the highest known temperatures, much higher than any temperatures of combustion, and therefore producing the greatest fluidity of flux and metal, and this without introducing air or fuel, but, on the contrary, maintaining a perfectly neutral atmosphere above the metal and slag. While the high fluidity of metal and slag conduce to the most rapid, uniform and chemically perfect action on the part of the absorbing flux, no oxidizing products, nitrogen or other impurities of combustion can enter the metal, and the whole operation can be continued as long as the operator desires, introducing or removing any ingredients, and in exact percentages.

Furthermore, irons and steels of specifications which have been obtained with difficulty, or never have been obtained in any of the standard processes, are readily obtained in the electric furnace. For instance, nickel steel, which Mr. Schwab is quoted as stating will be the steel for rails in the future, can be made directly without difficulty in the electric furnace. The superior control of the electric furnace over all furnaces depending in their action on heat of combustion especially commends its use in the refining of high-grade irons and steels.

The extent to which the electric furnace will be generally introduced depends on the cost of operating the electric furnaces and the superiority of the product as compared with that of combustion furnaces. The cost of electric heat obviously depends upon the cost of power from water or other sources, as compared to the cost of fuel at the locality under discussion. Further, electric energy may be supplied from water power or from blast furnace gas at a cost, when the efficiency of the electric furnace is considered, which compares favorably with the cost of high-grade fuels such as charcoal and producer gas.

Prof. J. W. Richards has pointed out, in his excellent paper on "Electric Furnace Reduction of Iron Ore," presented at the Niagara Falls meeting of the American Electrochemical Society in

May, 1909, that the amount of fuel used in a blast furnace is determined by the amount which must be burned at the tuyeres to produce the necessary smelting temperature, and not by the amount necessary to perform the reduction of the metallic oxides. The amount necessary for performing the reduction taking place in the furnace is only one-third to one-half of the amount necessary to burn to provide the smelting heat, and he is confident that any practical method of introducing electrical heat into the crucible of a blast furnace will result in large economies in the furnace working. Only one-fourth of the heating power of the fuel is developed in the region around the blast tuyeres, and yet if half of this could be replaced by electrically generated heat, an economy of 50 percent could in all probability be reached upon the fuel bill. It takes 1.2 tons of coke to make a ton of pig iron in the blast furnace, and about ¾ of a ton is burnt by the blast, producing in the melting zone about 25 per cent. of the calorific power of the coke. If one-half of this smelting heat, or 12½ percent of the actual heat of combustion of the fuel used, could be supplied by electric energy, the coke required could be reduced one-half, or 0.6 ton per ton of pig iron. The quality of the pig iron would also undoubtedly be greatly improved, and it is probable the output would be increased.

There are two general types of electric furnaces used in metallurgy.

The first are called arc resistance furnaces, because the heat is mostly developed in an arc established between two large carbon or graphite electrodes, or between these electrodes through the slag and metal bath.

The second are called induction furnaces, because the melted metal forms a single-turn closed-circuited secondary of a large transformer.

The arc resistance furnace is adapted to both the reduction of iron ore to pig iron and also to the refining of pig iron and steel.

The induction furnace is only adapted to the refining of metals, and cannot well be used for the reduction of ore.

Among the many designs of these two general types of furnaces, I will refer briefly to the following:

The Frick Electric Reduction Arc Furnace for Smelting Iron Ore.

Capacity, approximately 25 tons of pig iron per 24 hours; current taken, 2,000 kw., or approximately 1 kw. hour per pound of pig iron produced. Where iron ore used is of not less than

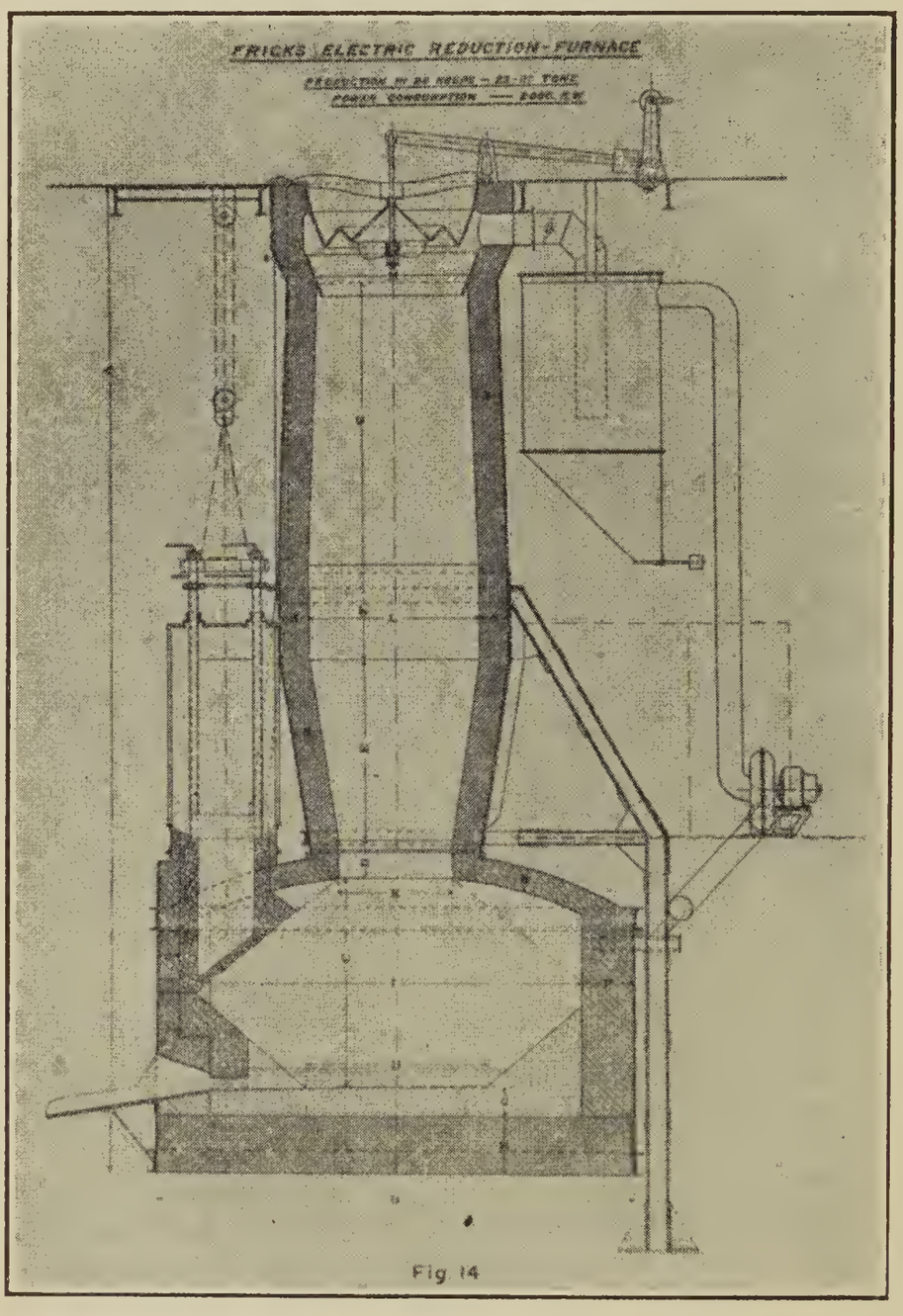


FIG. 1. Frick Induction Smelting Furnace.

57 percent Fe, the theoretical power required for the reduction of the iron in the presence of carbon and unslacked lime is from 1,200 to 1,350 kw. hours per ton, exclusive of the heat absorbed by the slag. This latter heat is from 100 to 300 kw. hours per ton of the pig iron, making a total of from 1,300 to 1,650 kw. hours per ton, provided burnt limestone is used.

The radiation losses occur partly through the walls, partly through the electrodes. In the case at hand the radiation losses are said to be from 320 to 370 kw. hours. The electrical efficiency of this furnace is therefore approximately 80 percent.

Smaller furnaces have larger radiation losses and lower efficiency.

The Frick Induction Type Furnace for Refining Iron and Steel.

This furnace consists of a ring-shaped crucible of uniform cross-section holding the melted metal and forming the secondary of the transformer; a magnetic core, built of laminated iron, forming a closed magnetic circuit around the coils, and two primary coils of insulated copper ribbon, mounted one above and

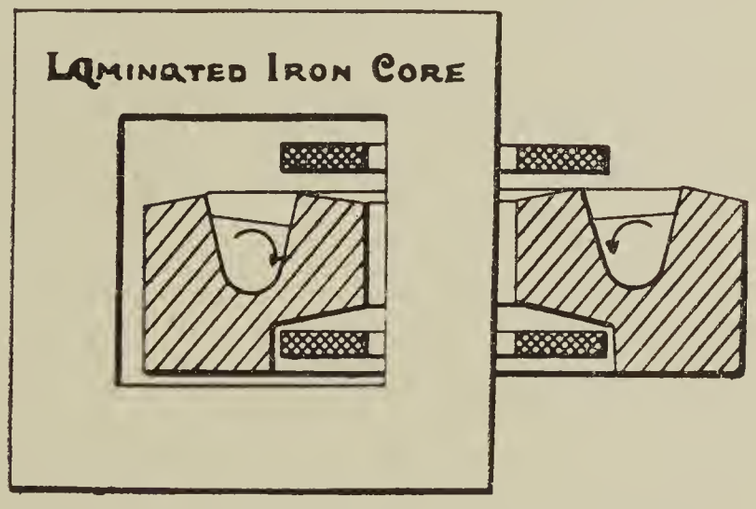


FIG. 2. Principle of Frick Induction Furnace.

one below the crucible on the magnetic core. These coils may be wound for any desired voltage up to, say, 6,600 volts—5,000 volts, I believe, is used in the furnace shown in the lantern slides. This furnace was built by Mr. Frick for the Messrs. Fried Krupp, A.G., in Essen, Germany, last January, and has been in successful operation since, refining approximately 20 tons of steel per day from cold scrap, in three charges, in about 6½ tons per charge of 6½ hours' duration on charge. The power required is approximately 1 kw. hour for 3 pounds of steel refined, or 665 kw. hours per ton. To obtain a reasonably high power-factor, a special low-frequency alternating current of from 5 to 15 cycles is used. An engine-driven generator designed to furnish this low-frequency single-phase current is employed. The

electrical power supplied is controlled by regulating the generator voltage. The electric efficiency of this furnace is said to be about 65 percent.

The power consumed in melting the material (cold iron and slag) to, say, 1,500° C. in a 10-ton furnace is approximately 600 kw. hours per ton, or 0.3 kw. hours per pound. The power

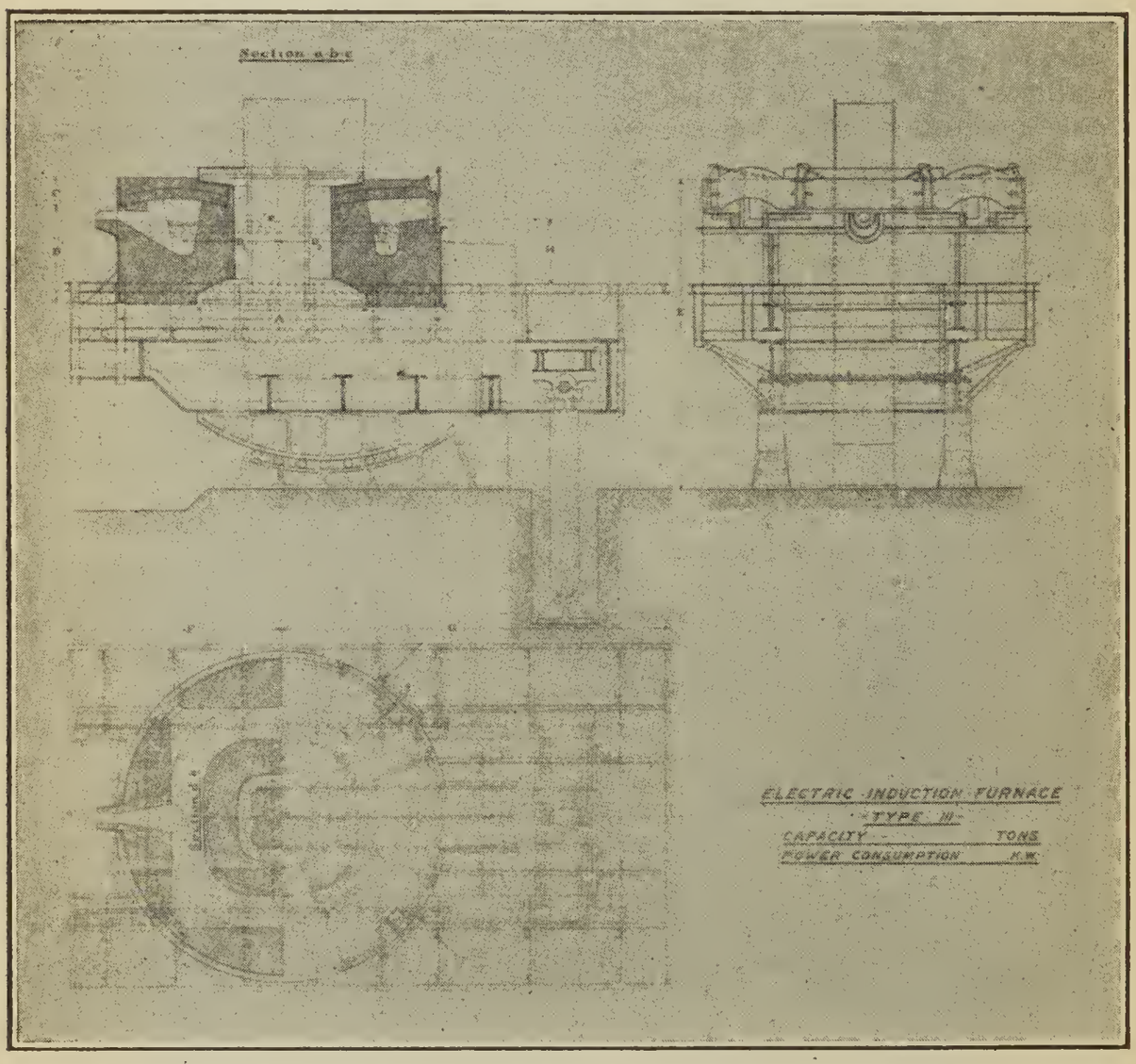


FIG. 3. Frick Induction Furnace.

consumed for refining the steel after melting is from 1,800 to 2,000 kw. hours for a 10-ton charge, or approximately 0.1 kw. hour per pound. Therefore, only where cheap power is available can the electric furnace be commercially used to melt cold material. The melting-down can be effected more economically in the open-hearth or other combustion furnace.

It is estimated that in a well-designed 15-ton, 2,000-kw. induc-

tion furnace the total thermal efficiency from coal or gas would be approximately as follows:

Gas engines, say, 20 percent.

Electric generator, say, 94 percent.

Electric furnace, say, 80 percent.

Total efficiency, 15 percent.

If steam turbine generators are used at, say, one-half the cost for fixed charges over the gas engine installation and, say, 15

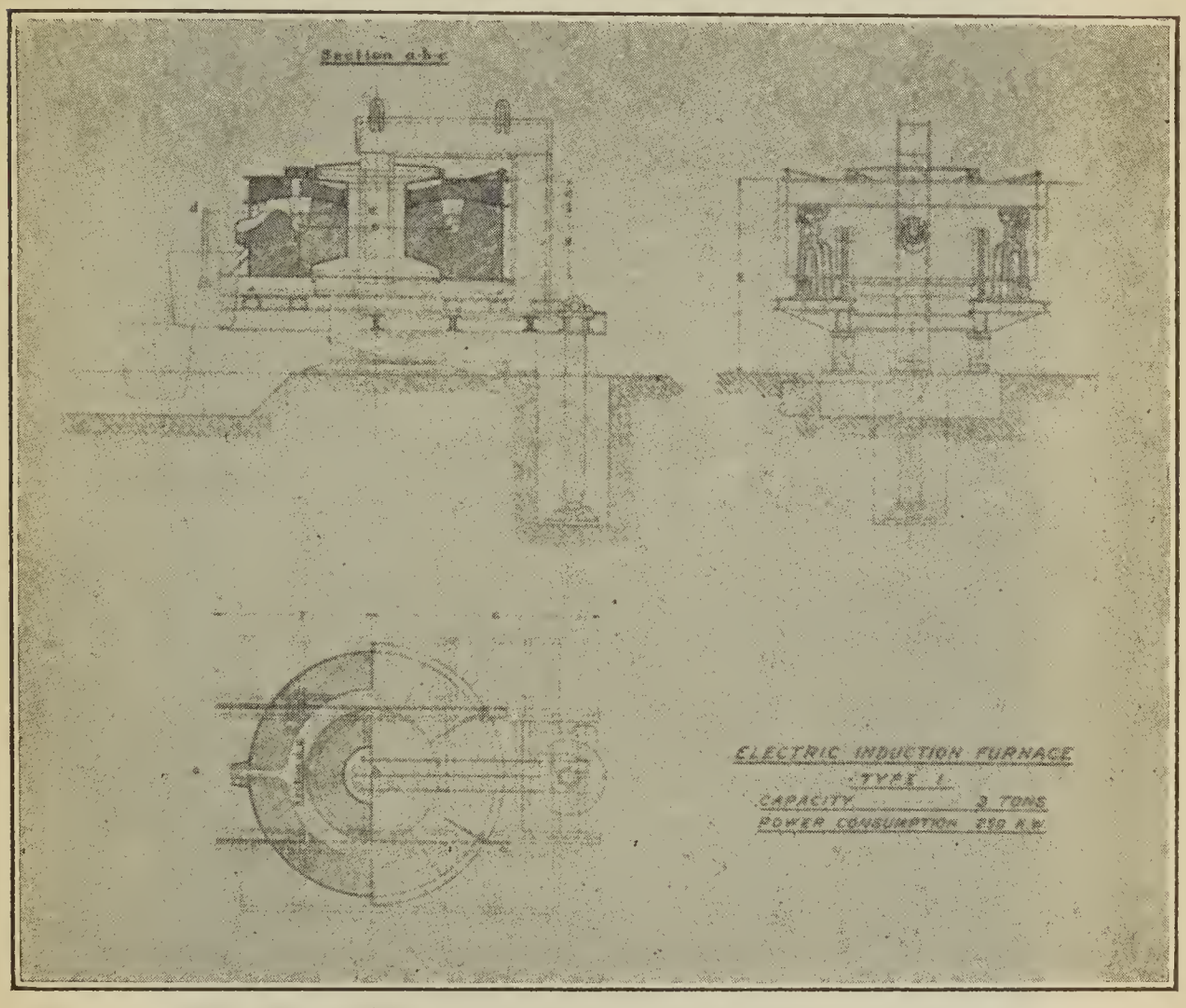


FIG. 4. Frick Induction Furnace, with Revolving Cover.

percent efficiency from the coal or blast furnace gas, the total thermal efficiency of the electric furnace would be 11 percent.

The efficiency of an open-hearth furnace is said to be from 20 to 25 percent. In this case the fixed charges and maintenance of the gas producers partly offset the turbines or gas engines. It is therefore apparent that the cost of refining melted pig iron or steel in the electric furnace, while considerably greater than by the open-hearth, is not excessive.

The Héroult Furnace.[1]

The most notable installation of the Héroult arc resistance furnace for the reduction of iron ore to pig iron is that of the Noble Electric Steel Company, at Héroult, California. In 1907 the first large furnace was built, taking 1,500 kw.; but, not prov-

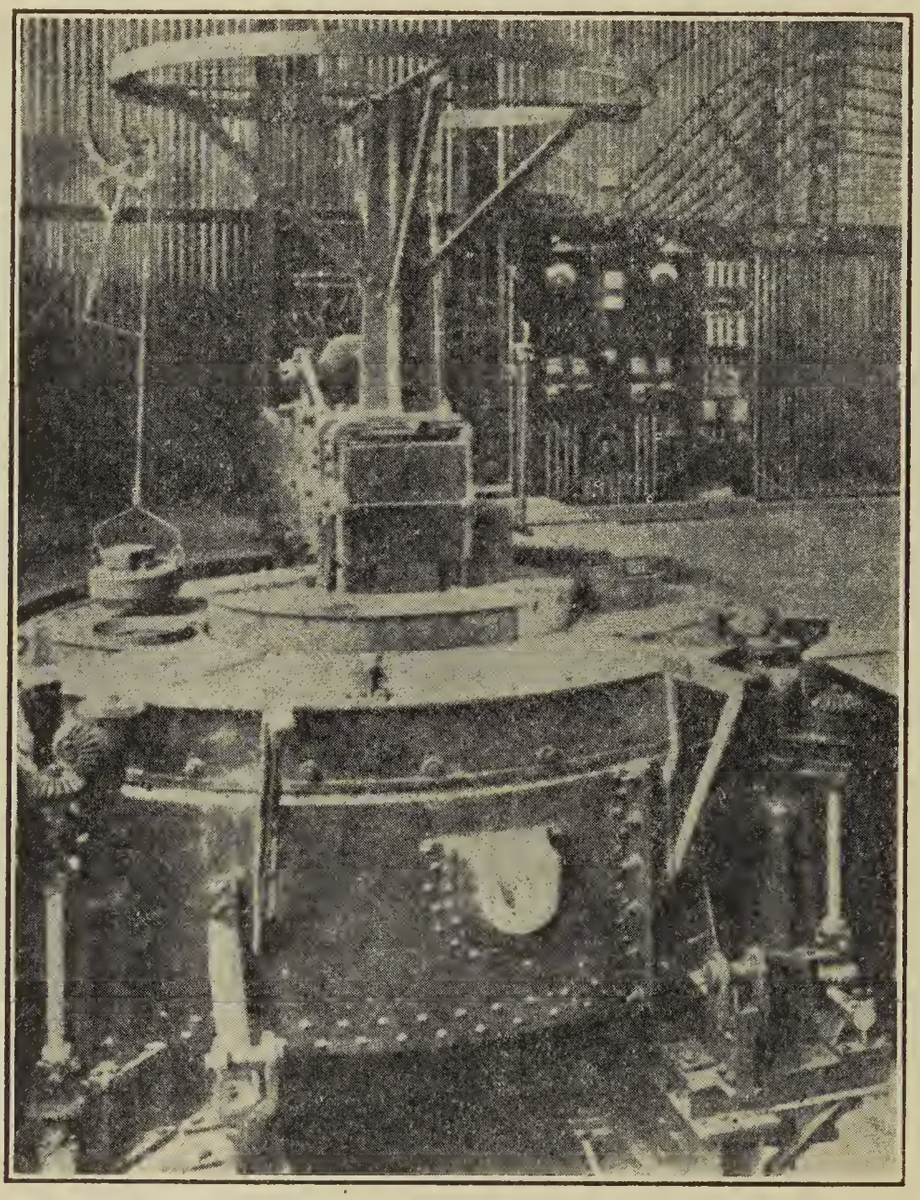


Fig. 5. Frick Induction Furnace, with Revolving Cover.

ing entirely successful, this furnace was replaced with a smaller experimental furnace of 160-kw. capacity. From the experience obtained with this furnace, a second large furnace was built early in 1909, which has been in almost continuous service since then, making 25 tons of pig iron per day of a quality comparable with

[1]For further description and illustrations of the Heroult Furnaces, see Transactions of this Society, Volume XV, 1909.

the best Swedish. Four more furnaces of the same size are now being built, which will make this the largest plant of the kind in the world.

A very pure magnetic ore of 70 percent Fe and a high-grade limestone are quarried nearby. The company makes its own charcoal and purchase hydro-electric power from the Northern California Power Company. Three 750-kw. oil-insulated water-cooled 60-cycle transformers are wound for 2,200 volt primary and a secondary range of 35 to 75 volts. The secondary current varies from 10,000 to 21,400 amperes. The range in voltage is controlled by a dial switch in the primary circuit of each transformer, giving steps of about 3 volts in the secondary. The generation of energy in the furnace is, therefore, controlled externally without movement of the electrodes, whose position is changed only to accommodate their wear in the crucible of the furnace. There are six electrodes, two for each transformer. While the primaries of the transformer are connected to the three-phase power line, the secondaries are not interconnected.

There are some 30 Héroult arc resistance furnaces for the refining of steel in service in Europe and America, in sizes from 1 to 15 tons per charge. One of the largest of these is installed in the South Chicago works of the Illinois Steel Company. This furnace has been in regular service for more than a year, refining blown Bessemer metal to a wide variety of specifications. Power is supplied from 3-phase, 25-cycle, 2,200-volt circuit. The furnace has three electrodes connected delta to the secondaries of the transformers. They are each counterweighted and are raised or lowered by a motor-driven mechanism which is either automatic or hand-controlled.

Induction Electric Furnaces.[2]

The Kjellin and Röchling-Rodenhauser furnaces are the most noted induction furnaces. The first one was built by Mr. Kjellin, in February, 1900, in Gysinge, Sweden. Thirty of these furnaces are now in regular operation in different parts of Europe. Electric heat is not only supplied through the metal bath acting as a short-circuited secondary, but also from a special secondary

[2] For further description and illustrations of Induction Furnaces, see these Transactions, Volume XV, 1909, and Volume XVIII, 1910.

winding, which supplies current to metallic plates embedded in a conducting mixture of refractory material which forms a part of the lining of the furnace. The current from these plates passes through the lining, then through the melted metal in the main hearth of the furnace. This design greatly improves the action and raises the power factor of the current taken by the furnace.

The Keller furnace for the refining of steel, six of which are in satisfactory operation in France and Germany, is also shown in detail in the references given.

The demand for strictly high-grade steel, absolutely homogeneous and of finest grain, is today coming from the railroads for steel rails and structural bridge steel, from the government for armament, from the automobile industry, from every manufacturer of tools and machinery, engines, steam turbines, electrical manufacturers and, indeed, every manufacturer using iron or steel. The treatment of Bessemer and open-hearth steel in the electric furnace at an increased cost entirely within the limits of the purchaser will make this steel comparable in its fineness with crucible steel, and have the physical characteristics best adapted to the particular application desired. Since the railroads have investigated the causes of rail breakages, it has been proved that many of them were due to the presence of foreign injurious bodies, such as slag, manganese sulphides, etc. The possible presence of these impurities, as well as the products of oxidation and nitrogen, is inherent in the Bessemer and open-hearth furnace product, but can be almost entirely eliminated by a treatment of an hour or two in the electric furnace.

Rails from electric furnace steel are now being tried out on curves, railway crossings and points where the service is most severe, by a number of the large railway systems. These rails combine unusual tensile strength, toughness and hardness. Their life alone, aside from their increased reliability, will probably justify the increased cost.

To bring the enormous output of steel rails, structural, merchant and plate steel up to the high grade of crucible steel will mean a new era for the steel business and rapid advances in all lines of manufacture employing iron and steel.

The manufacture of modern and light-weight steel castings has always been a difficult and unsatisfactory problem. There

is a large wastage, particularly in castings of odd shapes. This is principally due to impurities and sluggishness of the flow of metal in castings. With less than one-third the electric power necessary for purification, the liquid metal can be held indefinitely in an electric furnace without any loss in its composition or danger of burning, and a highly liquid metal can be cast uniformly free from impurities and gases. Such steel castings can in a large measure replace the steel forgings at present used, at a much reduced price. While the large steel companies will, no doubt, introduce electric furnaces as a refining means for their principal output, the electric furnace can probably be used to advantage by manufacturers of all kinds of iron and steel products in making special high-grade steels from their waste scrap iron and steel, including borings and turnings, as it accumulates in process of manufacture. These furnaces will either be entirely electric or the metal may be brought to the melting point by gas or coke fuel and then treated by electric heat.

As electricity has revolutionized our means of communication through the telegraph and telephone, displaced gas and other illuminants for lighting, supplanted the horse on the tramcar and mechanical drive in industrial plants, even driving the rolling-mill machinery in the steel plants and the hoists in the mines, in such instances working a wonderful transformation, so, in entering this new field, we may anticipate equally marked advances and a very great resultant demand for electric power and electrical apparatus.

An illustrated lecture delivered before the Chicago Section of the American Electrochemical Society, January 20, 1911. Also called up for further discussion at the Nineteenth General Meeting of the Society, in New York City, April 8, 1911, President Wm. H. Walker in the Chair.

A FEW EXPERIENCES WITH THE 15-TON HEROULT ELECTRIC FURNACE AT SOUTH CHICAGO

By C. G. Osborne.

The 15-ton Héroult arc furnace at South Chicago has now been in more or less continuous operation since May 7, 1908, a period of over a year and a half, and, therefore, a few experiences of those who have been interested in these operations will perhaps be of interest to those gathered here to-night.

DESCRIPTION OF FURNACE.

Many of you have visited the South Works of the Illinois Steel Company and have seen the furnace there. To these a description of the furnace will mean nothing; but there must be a number here tonight who are not acquainted with the details of its construction and operation, and it is for these that this brief description is intended.

Fig. 1 gives an idea of the foundations of the furnace, etc. Upon a solid foundation about 5 feet (1.55 meters) above the ground-level, a stationary rack 8 feet 9 inches (2.6 meters) long is fastened. Upon this rack the furnace proper rests on a floating pinion, fastened to its shell by rivets. The arc of this floating pinion has a radius of 10 feet (3 meters), and aims to give the furnace an angle of approximately 29° when tilted over to its full extent.

Attached to the extreme back of the furnace (as shown in Fig. 2) is an 18-inch plunger with a 4-foot stroke, working in a cylinder attached to a hydraulic line of 500 pounds' pressure to the square inch (34 atmospheres). This gives a lifting power approximately of 45 tons. The balance of the furnace is so arranged that the equilibrium is never upset, and therefore to return to a horizontal position merely requires the releasing of

the pressure, and the furnace returns of its own weight. It will be readily seen that the floating pinion and rack work requires some provision for the forward position of the furnace when

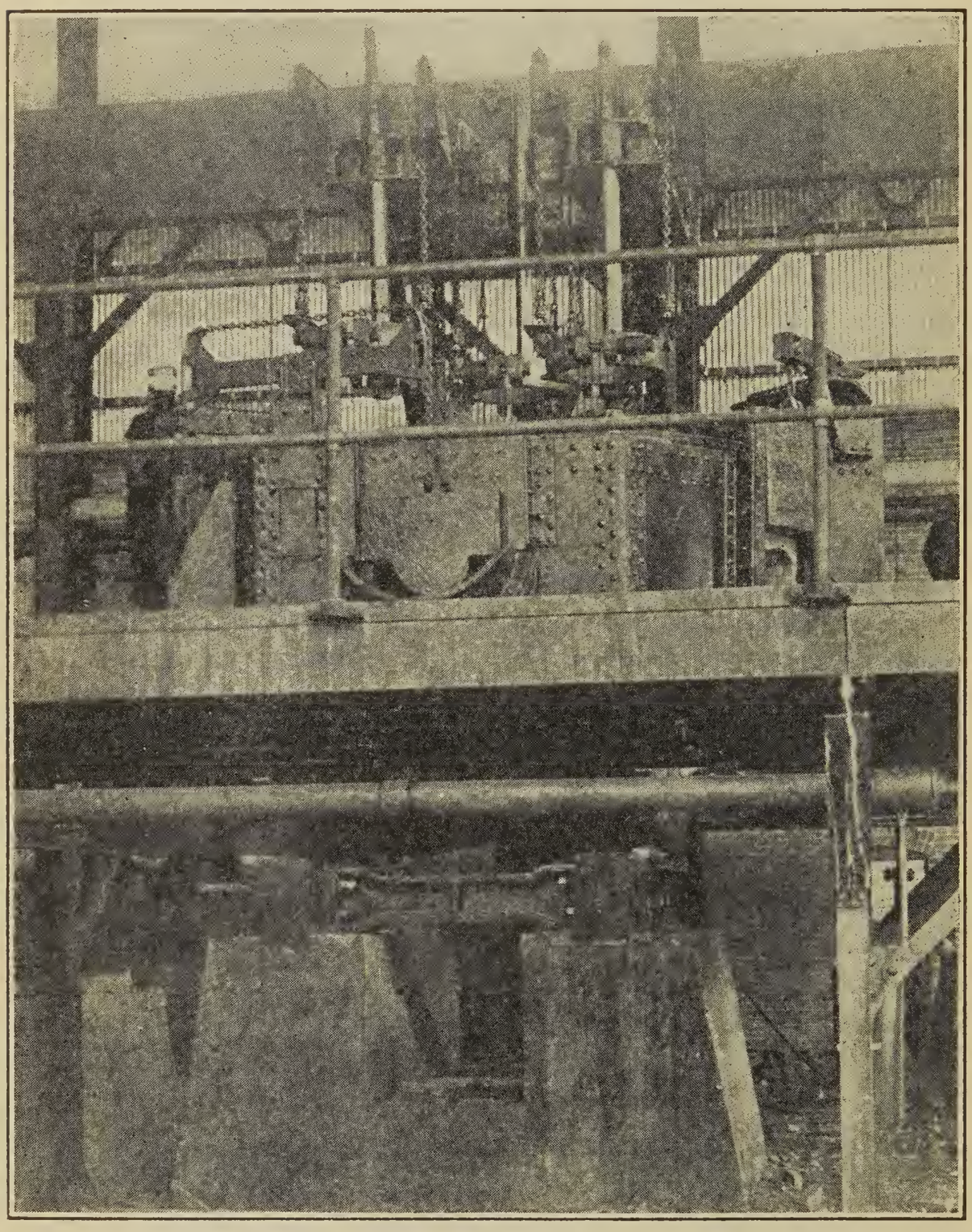


Fig. 1. Front View of Furnace, Showing Foundations.

tipping. This is taken care of by having a movable cylinder pivoted at both the top and bottom, which allows the cylinder to follow the motion of the furnace.

The Furnace Proper.

The furnace shell is of plate steel, 1 inch (2.5 cm.) in thickness, riveted together. The outside horizontal cross-section plan is approximately that of a complete circle of 13½ feet (4 meters)

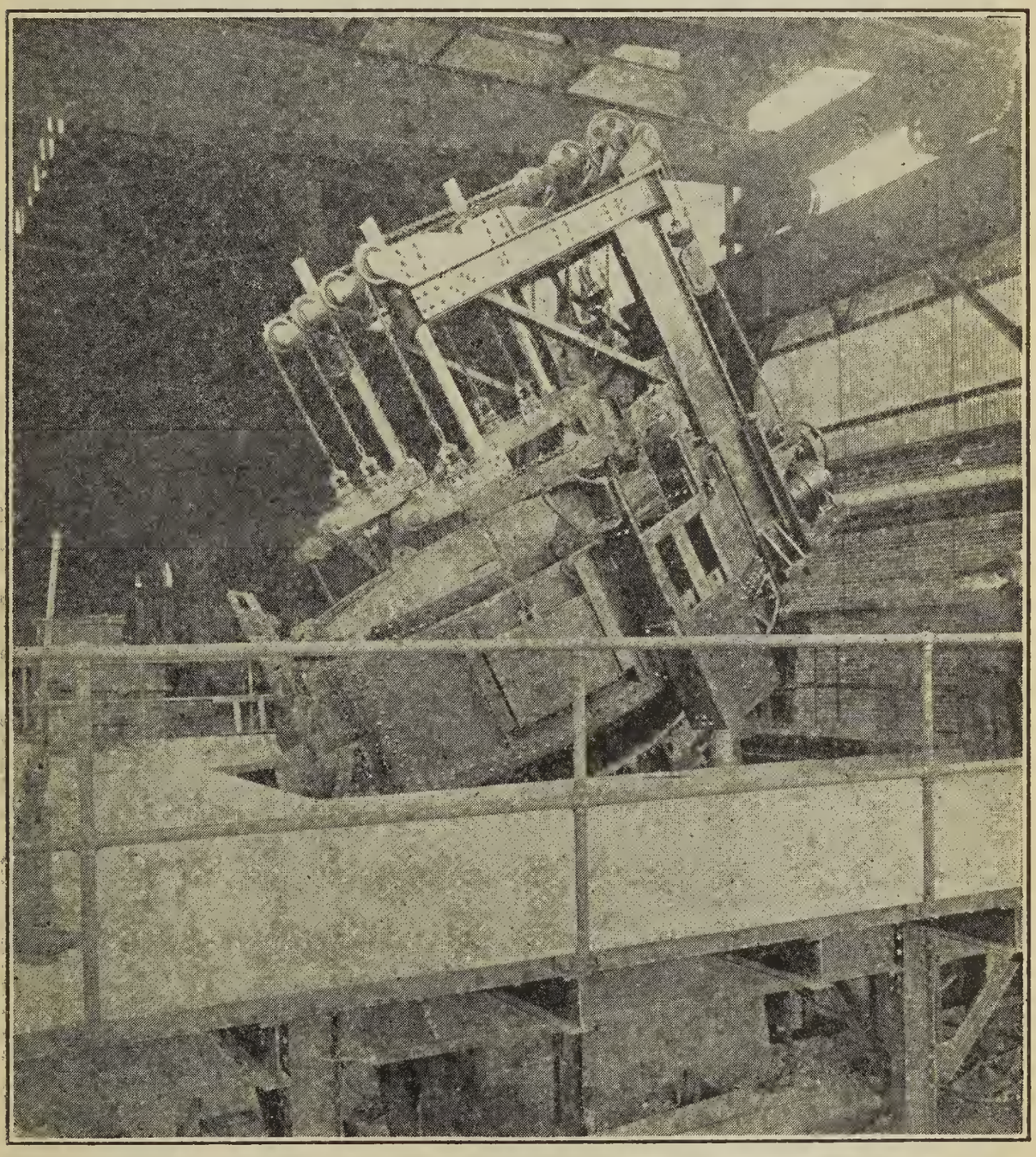


FIG. 2. Side View, Showing Furnace Tilted.

in diameter, with two flattened portions situated at the front and back respectively.

On the bottom of the furnace, within the 1-inch plate, and next to it, one row of magnesite brick, laid the 4½-inch (11.5 cm.) way, is placed across the flat portion.

The side walls of the furnace are vertical and consist of two rows of magnesite brick, laid the 9-inch (22.5 cm.) way, giving

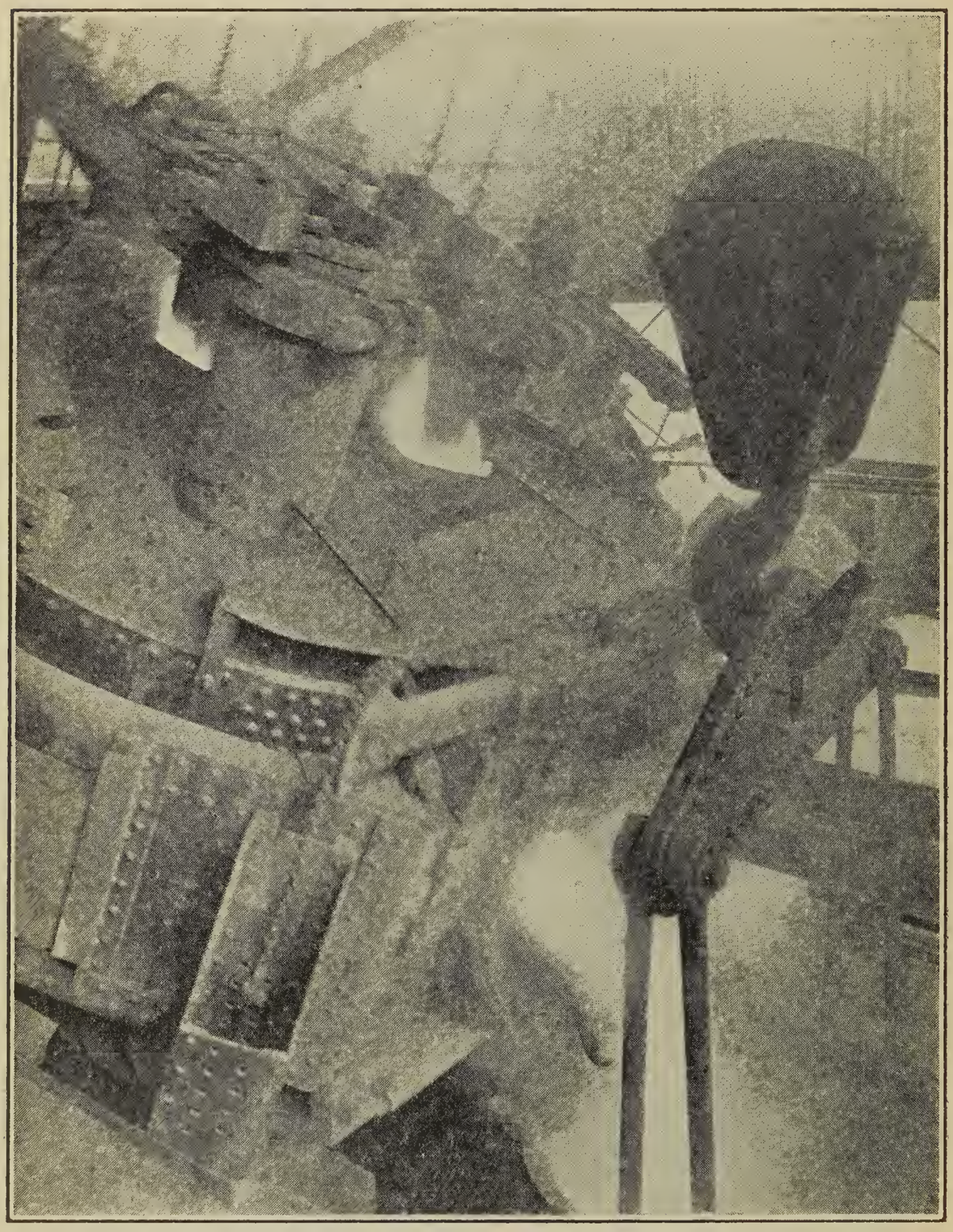


FIG. 3. View from Furnace Platform, Showing Heat Tapping.

a thickness of 18 inches (45 cm.) of magnesite brick. These solid magnesite brick walls extend up to the furnace roof.

The bottom "proper" of the furnace consists of dead-burned

Spaeter magnesite to a depth of 12 inches (30 cm.) at its thinnest point, which is, of course, at the extreme center. From this thinnest point the bottom slopes gradually upwards so as to form a portion of a sphere 7 feet 2 inches (2.15 meters) in radius.

To diverge a moment from the construction of the furnace, this bottom was put in in the following manner: Dead-burned

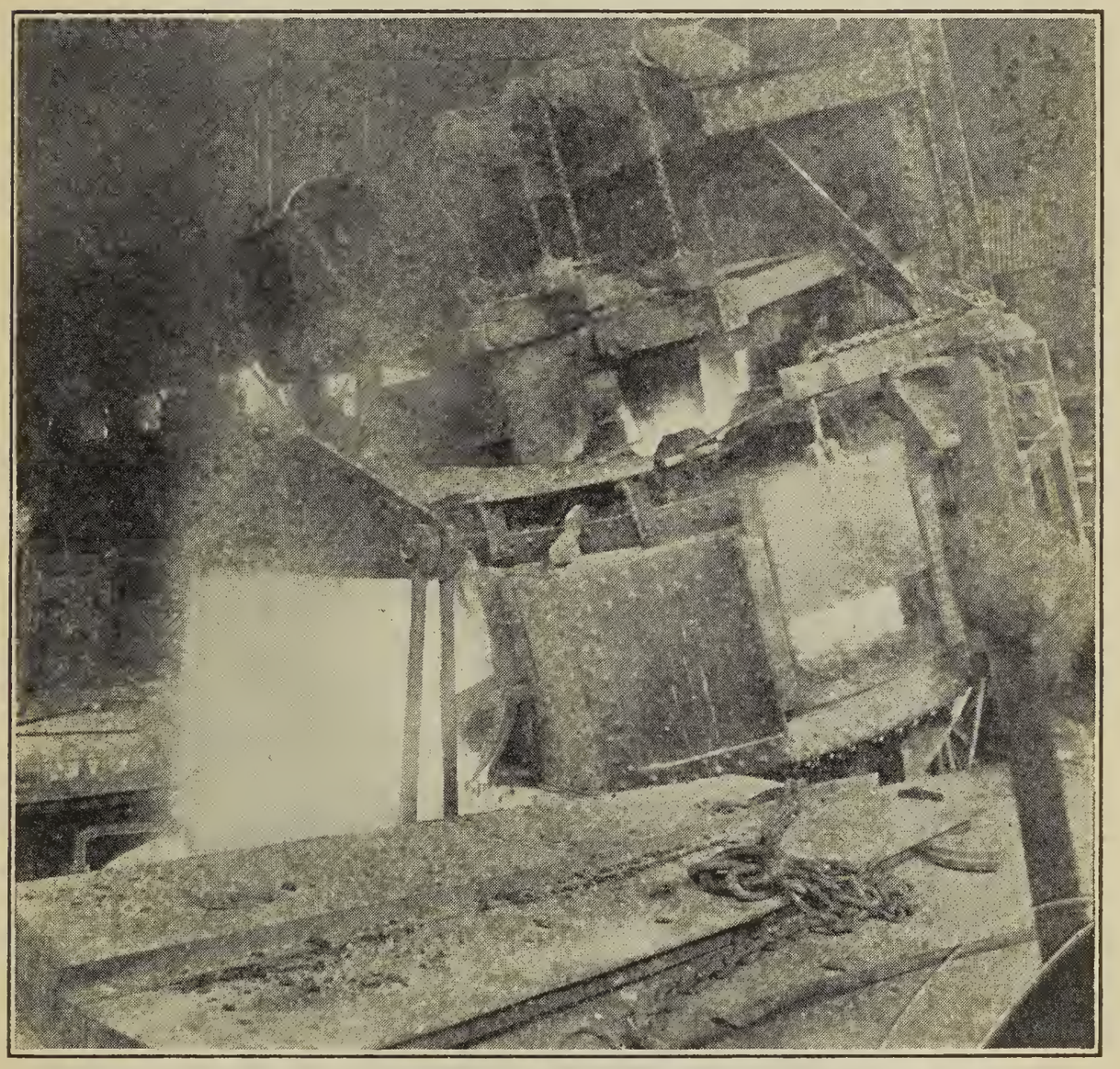


FIG. 4. View from Furnace Platform, Looking North.

and carefully ground Spaeter magnesite was mixed with basic open-hearth slag in the proportion of four of magnesite to one of open-hearth slag. To this mixture, sufficient tar was added to make the mass sufficiently plastic to enable it to be tamped into the furnace in the usual manner. The entire depth of the bottom was tamped in this way. Next, the furnace was filled with wood, dried out for about 48 hours, and then filled with

coke, and the electrodes lowered and the current turned on. In this way the bottom was fluxed into place.

The roof of the furnace can be seen in Fig. 3.

This furnace roof is of silica brick 12 inches (30 cm.) in thickness.

The roof is made up on a movable ring. This ring is fitted with a top and bottom angle iron to take a skew-back brick, and then from this the arch is spanned across the 10-foot (3 meters) interior of the furnace with an 8-inch (20 cm.) rise. The bricks are set in circles parallel to the steel ring, the usual wooden wedges being placed here and there to take care of the subsequent expansion of the brick. Holes for the electrodes are left in the roof by means of templates placed in position. The bricks are held in position around these holes by their lateral pressure.

There are five doors, two on each side of the furnace, and one in front over the pouring spout. These doors are of cast iron, lined with clay brick, laid the 4½-inch (11.5 cm.) way. They work in the usual groove arrangement, and are operated by steam pressure of about 150 pounds (11 kg. / sq. cm.). The front door over the pouring spout is an exception to this, being operated by hand with a counter balance.

The Electrodes and Their Handling Device.

The three electrodes are let down through the roof in the form of an equilateral triangle, each side of which is 5 feet 2 inches (1.55 meters) in length, the apex of this triangle pointing directly east, that is, towards the back of the furnace. The center of this triangle coincides with the center of the furnace roof.

The overhead structure which supports these electrodes may be seen in Fig. 4.

There are, of course, three separate holders, one for each electrode. Each holder is constructed of a solid copper casting bolted directly to the bus-bar. In front, these holders are split and joined with a right and left screw, which enables the holder to be opened or closed at will. The holders are designed to carry a 24-inch (60 cm.) electrode, but by means of contact blocks to fill, any smaller-sized electrode can be employed.

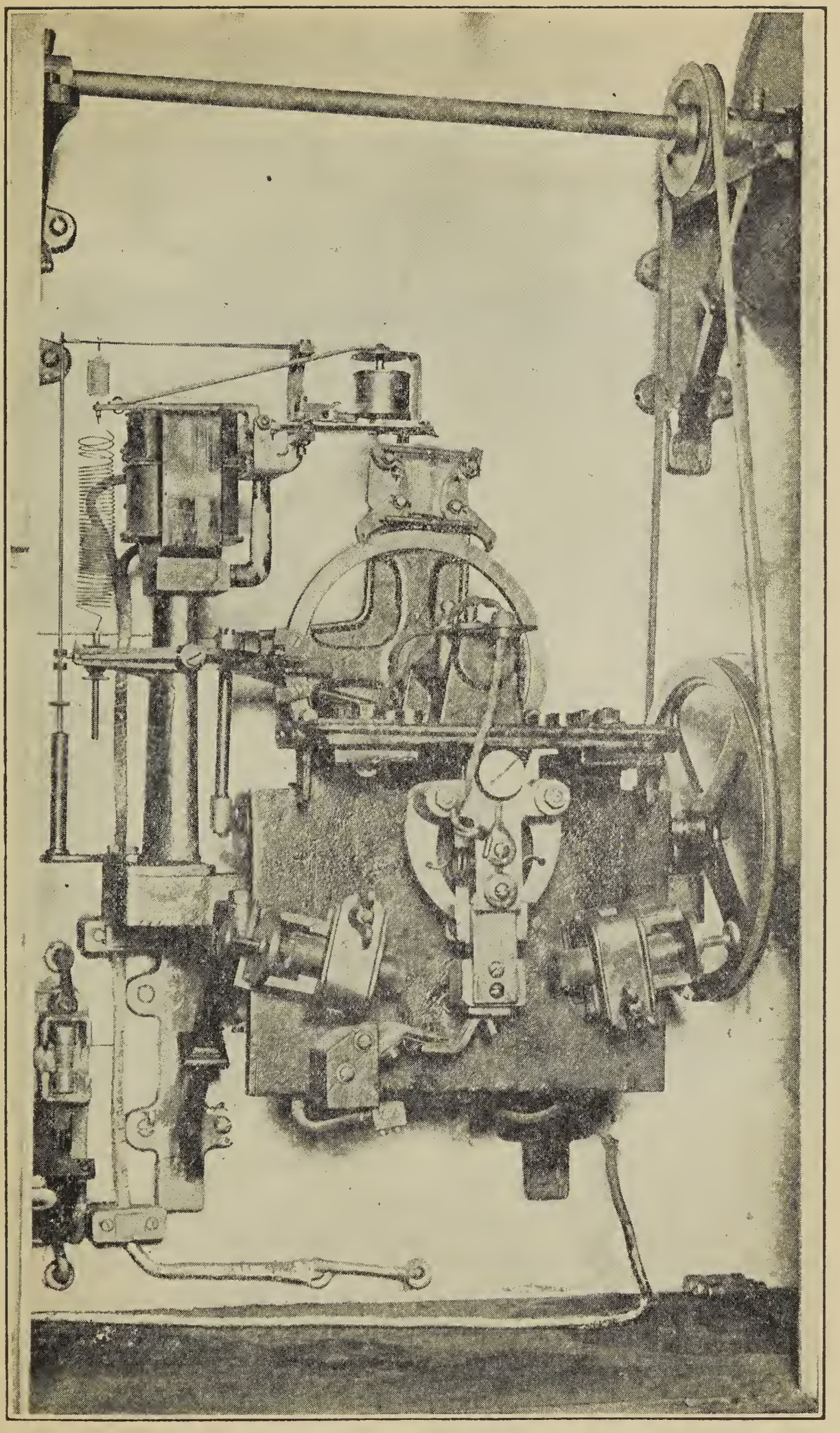


FIG. 5. Automatic Electrode Regulating Apparatus.

The weight of the electrode is supported by the chains (shown clearly on the picture). These chains run back over pulleys to the drums at the back of the furnace. These electrodes are kept in alignment by vertical guides.

The electrodes are regulated by individual motors placed at the back of the furnace. These motors are attached by gears to the drums. The regulation is by hand, by controllers, or by an automatic device.

It will perhaps interest you to dwell for a moment on this automatic regulation. Each electrode is, of course, regulated separately, and its regulation is as follows (Fig. 5):

A stationary magnet coil, the current through which can be adjusted at will, is opposed by a floating magnet coil, whose position is determined by a spring and the amount of current passing through it. The current in this floating magnet is obtained from a current transformer attached to the bus-bars. When the current in the bus-bars and the proportional current, therefore, of the floating magnet is that for which the regulator of the stationary magnet is set, the magnetic opposition of the two magnet coils is exactly counterbalanced by the strength of the spring, and the apparatus is at rest. When, on the other hand, the strength of the current in the bus-bars and, consequently, the proportional current in the floating magnet is either greater or less than that at which the stationary magnet is set, then the magnetic opposition of the two magnet coils either overcomes or is overcome by the strength of the spring, and the two magnet coils either retreat from or approach towards one another. This motion of the floating coil is transmitted by a lever, which in turn causes a dog to drop into a slot in a constantly moving rocker wheel, and in this way a right or left contact is made, and the motors controlling the electrodes, which, of course, work on direct current, are started, either clockwise or anti-clockwise, and the electrodes in turn are either raised or lowered. This is repeated with each oscillation of the rocker until equilibrium is restored. It might be of interest to state here that each contact made as spoken of above serves to raise or lower an electrode about $\frac{1}{8}$ of an inch. It has already been stated that the regulation can be by hand-controllers. These three hand regulators are situated at the back of the furnace at a

distance of about four feet. It is, of course, understood that the use of the hand regulators simultaneously disconnects the automatic regulators.

The operating platform of the furnace is about 9 feet (2.7 m.) from the level ground. Around the furnace on this platform, at

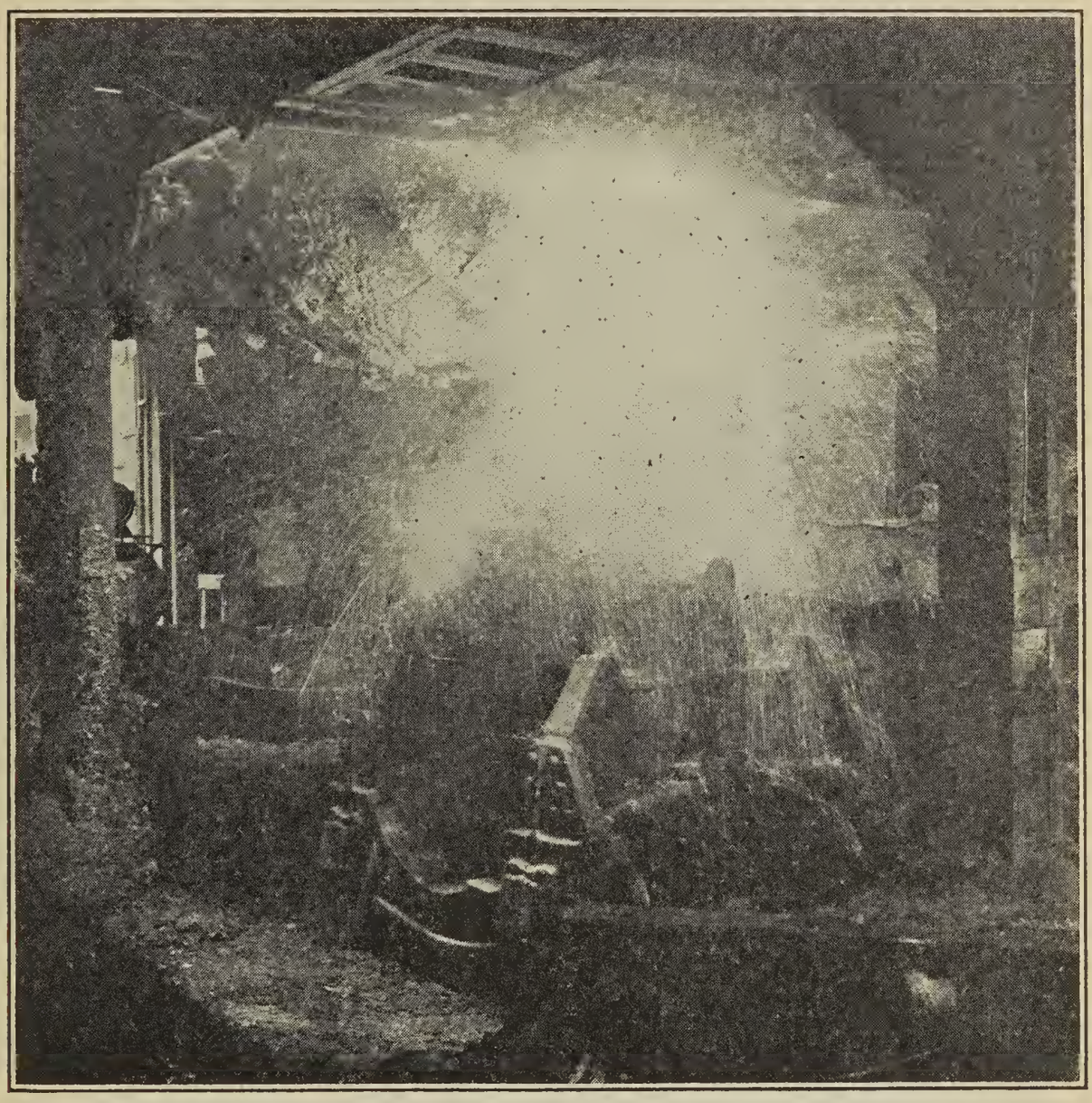


Fig. 6. View Showing Converter Pouring Metal to Electric Furnace Ladle.

convenient points, bins are placed for the miscellaneous materials used in furnace operation.

The front part of the furnace platform opens up to allow a ladle to be hung in position when the furnace is tapped and for any miscellaneous work in the pit.

The power for the furnace is generated by dynamos having as prime movers reciprocating gas engines, reciprocating steam

engines, high-pressure and low-pressure turbines. It is three-phase in character, 2,200 volts, and 25-cycle.

At the electric furnace it is stepped down by means of three 750-kw. transformers to the voltage of the furnace. These transformers are so arranged with switches that the primary turns may be altered to give a secondary voltage of 80, 90, 100 or 110 volts as desired. Ordinarily 90 volts is used.

The entire building is spanned by a 50-ton crane.

The pouring platform is situated to the south of the furnace.

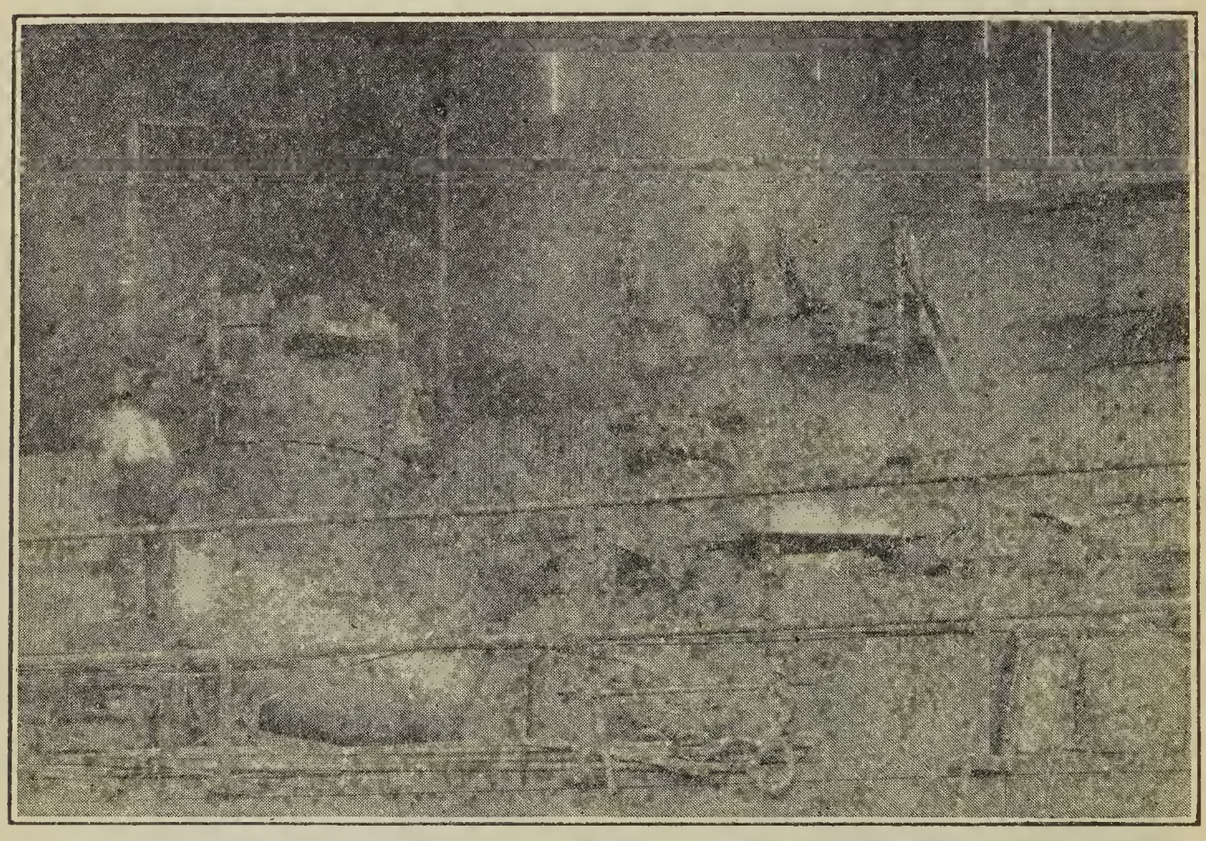


Fig. 7. View Showing Charging of Furnace.

It is 30 feet (9 meters) long, and enables eight molds to be placed in position for pouring.

THE OPERATION OF THE FURNACE.

The normal operation of the furnace is as follows:

Ordinary Bessemer pig iron is full blown in a 15-ton Bessemer converter, in from eight to twelve minutes. It is then poured directly from the Bessemer vessel to an electric furnace transfer ladle (see Fig. 6) and drawn to the electric furnace building, a distance of about ¼ mile (400 meters), in about five minutes. As a precaution against the possible formation of a skull in the

ladle, the Bessemer charge is blown about 1,500 pounds (680 kg.) of scrap "hotter" than ordinary Bessemer practice.

Immediately the ladle is received at the electric furnace it is picked up by the crane, slightly tilted, and the silicious slag is completely cleaned off by hand-rabbling. The metal is now ready

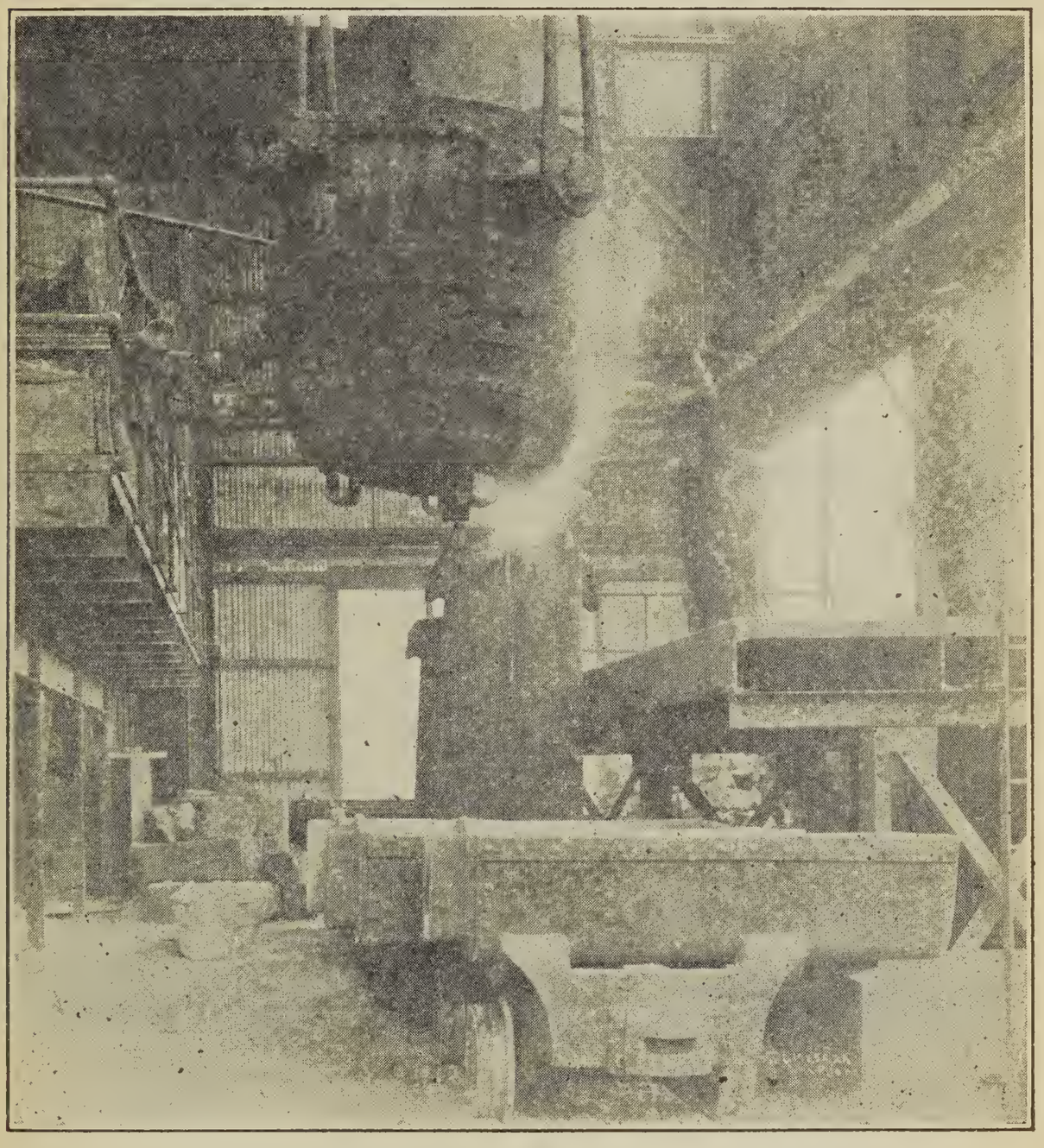


Fig. 8. View Showing Pouring of Heat into Molds.

for charging. To do this, the ladle is merely turned over on its trunions and the metal poured into a spout, through which it rushes to the furnace. This operation of cleaning off the slag and charging occupies from five to ten minutes. Fig. 7 shows another method of charging.

The electrodes are lowered and the current turned on.

As the metal is being poured into the furnace, the helpers shovel iron oxide and lime into the furnace through the working doors.

In this way a basic oxidizing slag is produced which serves to remove the phosphorus. In about thirty minutes this slag has served its purpose, and the furnace is tilted slightly forward and

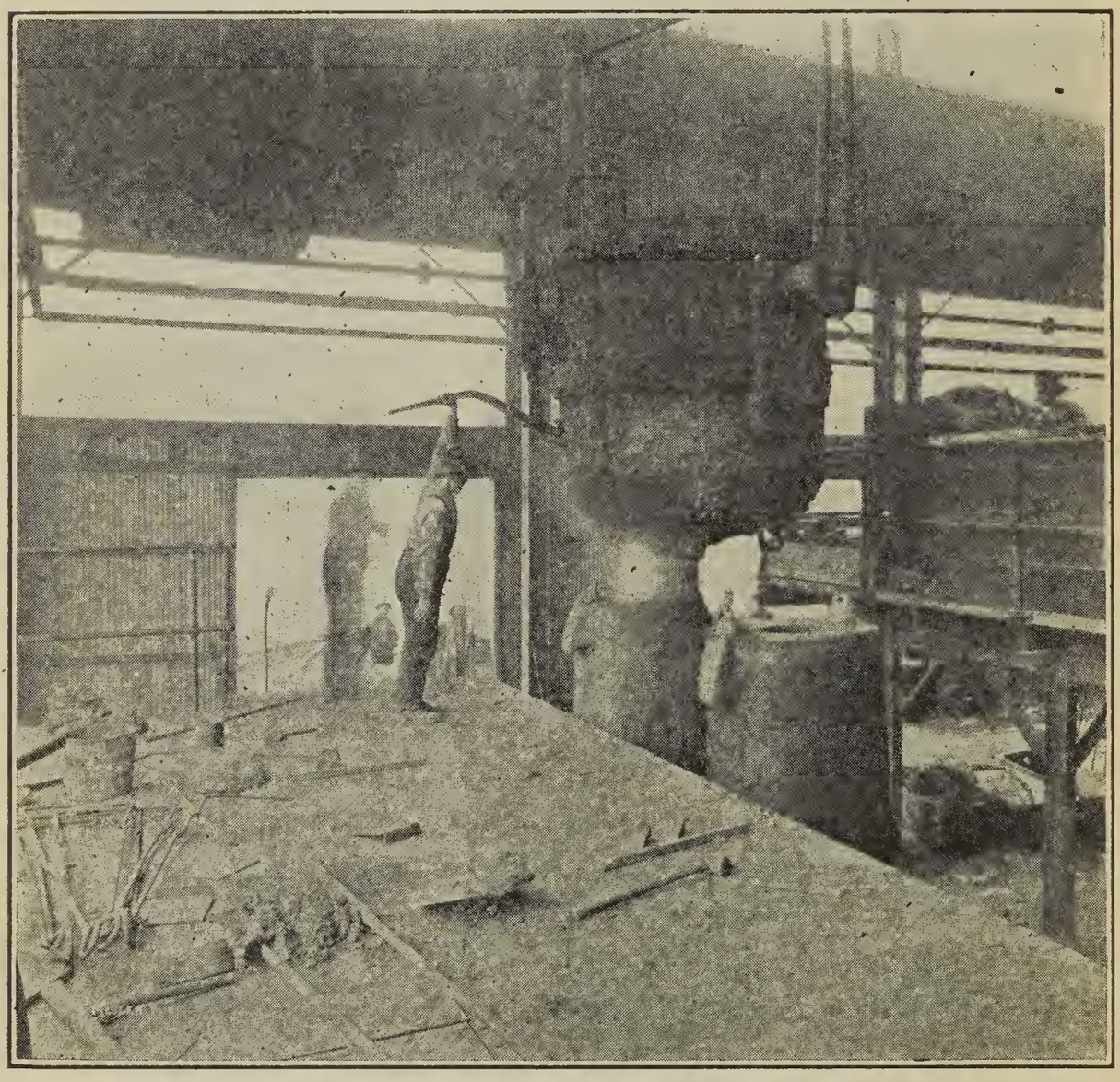


FIG. 9. View Showing Method of Pouring a Heat.

the slag removed in from five to ten minutes by hand-rabbling.

The recarburizer is added at this point. On the bare surface of the oxidized metal, lime is quickly added, with sufficient fluor-spar to keep the mass fluid. In about fifteen minutes this lime is melted, and finely divided coke dust is now thrown onto the top of the slag beneath each of the three electrodes.

Under the influence of the arc, calcium carbide is produced in gradually increasing quantities.

As soon as this state of affairs is reached, a neutral if not actually reducing atmosphere has been obtained. From here to the finish there is practically a dead-melt in a reducing atmosphere. The slag at this stage of the process is fluid and highly basic. If a sample should be taken and water added to it, the resultant acetylene gas, from the well-known calcium carbide and water reaction, is of sufficient quantity to light and burn for half a minute.

Tests are now taken to show the condition of the steel. A small cylindrical test piece is poured and forged to a round pan-cake-shaped object under a steam hammer located at the furnace. If this forged sample shows by its appearance a satisfactory condition of the metal, the bath is tapped. If not, further refining is necessary.

To tap the furnace, the electrodes are raised from the bath and the ladle swung by a crane under the pouring spout and the tilting lever pulled forward (see Figs. 3 and 4).

The pouring is done through a 1½-inch (4-cm.) nozzle to molds of varying sizes (see Figs. 8 and 9).

A typical furnace charge sheet is as follows:

ELECTRIC FURNACE CHARGE SHEET.

MATERIAL.	Lb.	Kg.
Bessemer blown metal	30,000	13,635
Scale	700	317
Ferro-Manganese, 80%	200	91
Ferro-Silicon, 10%	60	27
Ferro-Silicon, 50%	80	36
Recarbonizer	130	59
Fluor Spar	400	182
Coke Dust	200	91
Lime—1st Slag	600	273
Lime—2d Slag	600	273
Dolomite	400	182
Magnesite	25	11

Tapped previous heat	7.00 A. M.
Metal Ordered for	7.15 "
Metal Received	7.15 "
Began Fettling	7.17 "
Current on	7.27 "
Slag Off—Began	8.00 "
Slag Off—Finished	8.11 "
Tapped	8.48 "
Time of Heat	1 Hr. 21 Min.

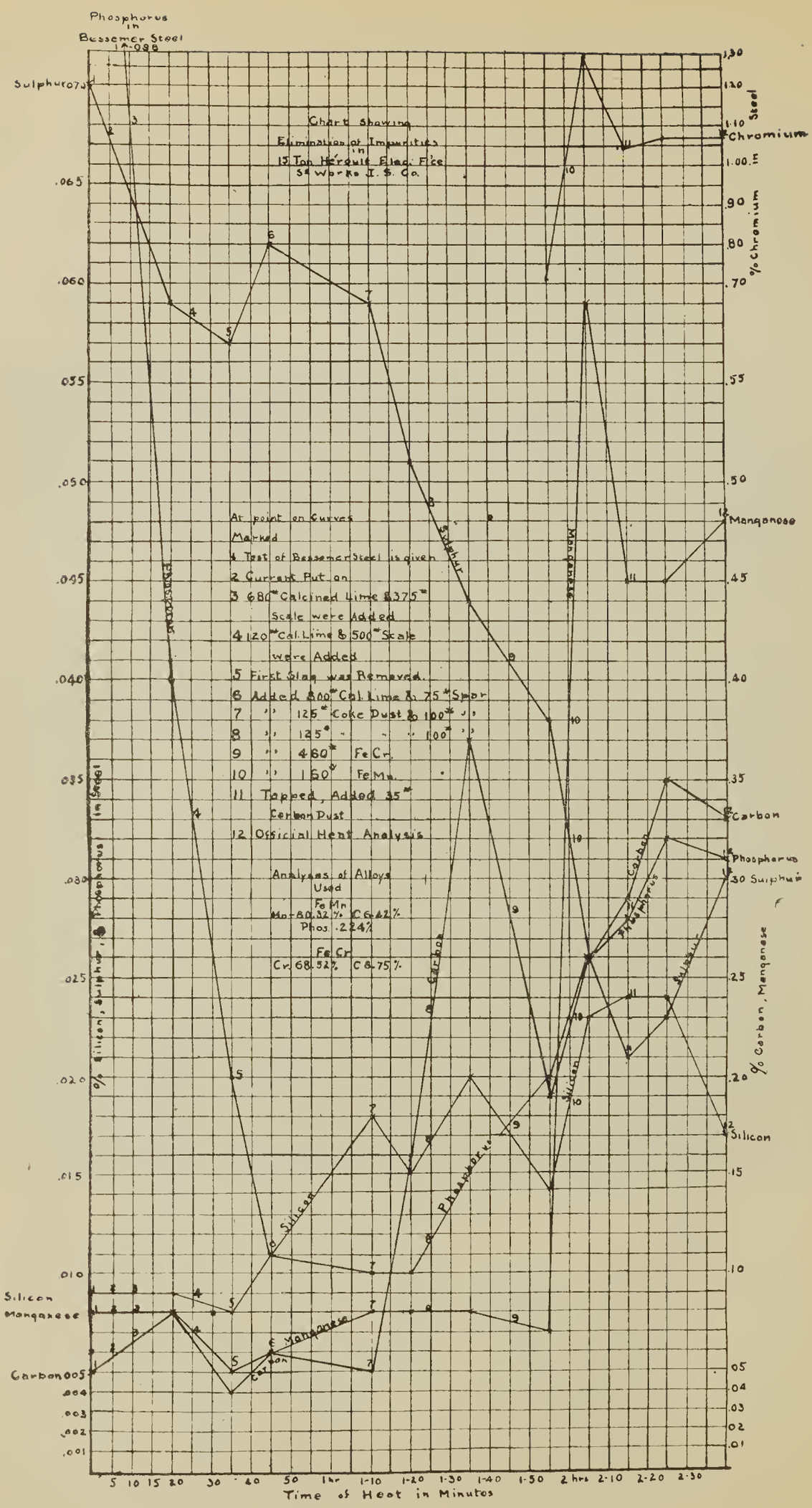


Chart Showing
Elimination of Impurities in
15 Ton Héroult Elec. Fice
St Works I. S. Co.
At point on Curves
Marked
1 Test of Bessemer Steel is given
2 Current Put on
3 680# Calcined Lime & 375#
Scale were Added
4 120# Cal. Lime & 500# Scale
were Added
5 First Slag was Removed.
6 Added 800# Cal. Lime & 75# Spar
7 " 125# Coke Dust & 100# "
8 " 125# " " 100# "
9 " 480# FeCr.
10 " 150# FeMn.
11 Tapped, Added 35#
Carbon Dust
12 Official Heat Analysis
Analyses of Alloys
Used
Fe Mn
Mn 80.32% C 6.42%
Phos .224%
Fe Cr
Cr 68.52% C 6.75%
Phosphorus in Bessemer Steel
1A-988
Sulphur
Phosphorus
Silicon
Manganese
Carbon
% Silicon, Sulphur, Phosphorus in Steel
% Carbon, Manganese
% Chromium Steel
Chromium
Manganese
Carbon
Phosphorus
Sulphur
Silicon
Time of Heat in Minutes
5 10 15 20 30 40 50 1hr 1-10 1-20 1-30 1-40 1-50 2 hrs 2-10 2-20 2-30

FIG. 10.

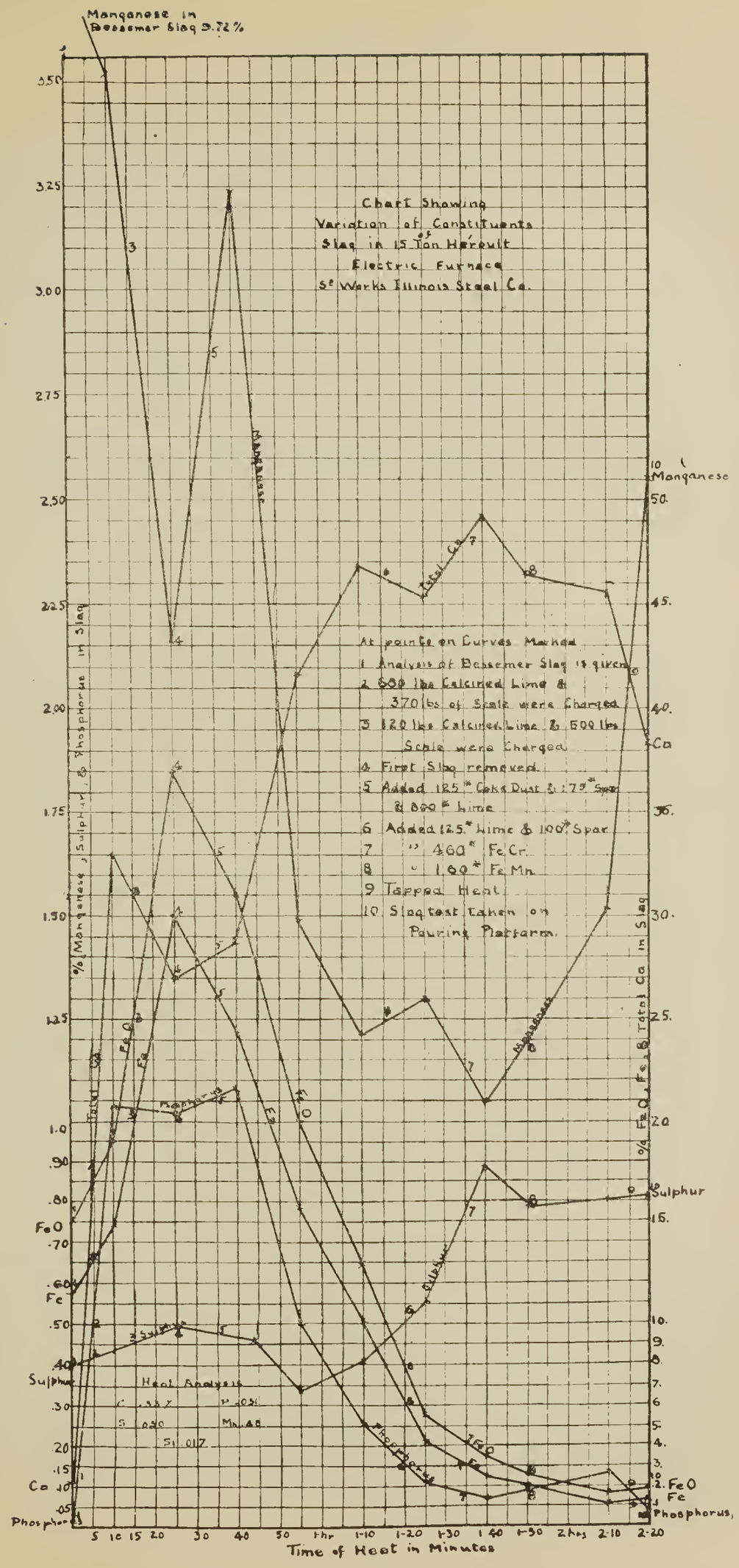

Manganese in Bessemer Slag 9.72%
Chart Showing Variation of Constituents Slag in 15 Ton Héroult Electric Furnace St. Works Illinois Steel Co.
At points on Curves Marked
1 Analysis of Bessemer Slag is given
2 600 lbs Calcined Lime & 370 lbs of Scale were Charged
3 120 lbs Calcined Lime & 500 lbs Scale were Charged
4 First Slag removed.
5 Added 185# Coke Dust & 175# Scale & 800# Lime
6 Added 125# Lime & 100# Spar
7 " 460# Fe Cr.
8 " 100# Fe Mn.
9 Tapped Heat
10 Slag test taken on Pouring Platform.
Heat Analysis
C .33 %
S .040
Si .017
Mn .48
P .021
% Manganese, Sulphur & Phosphorus in Slag
% FeO, Fe, & Total Ca in Slag
Time of Heat in Minutes
Manganese
Total Ca
Sulphur
Phosphorus
FeO
Fe
Ca
5 10 15 20 30 40 50 1hr 1-10 1-20 1-30 1-40 1-50 2hrs 2-10 2-20

FIG. 11.

It will be seen from this that it takes us an hour and a half to two hours to a heat, according to the grade of steel produced.

What is actually done in the electric furnace at South Works is to take oxidized blown metal of an approximate analysis of

C	*S*	*P*	*Mn*	*Si*
0.05-0.10	0.035-0.070	0.095	0.05-0.10	0.005-0.015

and produce deoxidized steel low in sulphur and phosphorus and, within reasonable limits, of practically any analysis required by the consumer.

Fig. 10 shows the elimination of the impurities in the electric furnace during the process of making an alloy heat. Fig. 11 shows the fluctuation in the slag analysis.

THE VARIETY OF PRODUCT.

The electric furnace at South Chicago has operated on a greater variety of product than any furnace in the world, and with bewildering intermingling of high-grade alloy steels, high-grade carbon steels and ordinary carbon steel. We have made of ordinary carbon steel rails of a dozen different sections, billets of all sizes and grades, plates of all sizes and grades, structural shapes, castings, small and large, high carbon and low, and forgings of all sizes; of alloy steels we have made nickel, nickel-chrome, chrome, manganese and silicon steels.

We have made a number of heats from cold materials. In several of these we took the worst scrap we could pick up—stove-plate scrap. With this stock, an axle heat was made which showed excellent physical tests. If I remember correctly, 77 blows from a 1,640-pound (750 kg.) hammer falling 43 feet (13 metres) broke the first axle, and 68 similar blows the second.

THE QUALITY OF THE STEEL.

The main chemical or physical characteristics in electric steel seem to be these:

A comparative freedom from oxidation.

A comparative freedom from segregation.

A higher tensile strength and slightly higher ductility for the same chemical analysis up to about 0.40 carbon, where the difference becomes less apparent.

STATEMENT OF AVERAGES OF ULTIMATE STRENGTH AND PERCENT ELONGATION (in 2 In. = 5 Cm.) OF ELECTRIC AND OPEN HEARTH PLATE STEELS—ARRANGED ACCORDING TO CARBON ANALYSIS

ELECTRIC PLATE STEEL						BASIC OPEN HEARTH PLATE STEEL					
Carbon Percent	No. of Heats	No. of Tests	Average Ult. Strength		Average Percent Elongation	Carbon Percent	No. of Heats	No. of Tests	Average Ult. Strength		Average Percent Elongation
			Lbs. Sq. In.	Kg./sq. mm.					Lbs. Sq. In.	Kg./sq. mm.	
0.08	3	5	59,194	41.4	27.25	0.08	3	5	51,690	36.2	32.00
0.09	2	5	59,502	41.6	27.25	0.09	2	5	52,570	36.8	32.00
0.10	3	5	57,662	40.4	29.20	0.10	3	5	54,666	38.3	29.90
0.11	3	5	59,585	41.7	27.65	0.11	3	5	54,854	38.4	30.65
0.12	2	5	64,080	44.8	26.05	0.12	2	5	56,510	39.6	29.70
0.13	3	18	65,880	46.1	25.90	0.13	3	18	56,595	39.6	28.54
0.14	3	12	62,030	43.4	26.43	0.14	3	12	55,322	38.7	28.64
0.15	3	15	61,203	42.8	26.70	0.15	3	15	58,683	41.1	28.21
0.16	5	27	69,220	48.4	25.25	0.16	5	27	52,901	37.0	28.61
0.17	5	22	66,638	46.7	25.03	0.17	5	22	55,780	39.1	28.81
0.18	5	21	65,330	45.7	25.44	0.18	5	21	58,469	40.9	28.31
0.19	3	15	70,336	49.2	23.83	0.19	3	15	59,504	41.7	27.50
0.20	2	7	72,853	51.0	22.82	0.20	2	7	58,294	40.8	28.82
0.21	2	9	68,640	48.0	25.16	0.21	2	9	63,050	44.1	27.00
0.22	1	2	70,820	49.6	25.75	0.22	1	2	54,500	38.2	29.75
0.23	2	7	73,370	51.4	23.53	0.23	2	7	61,148	42.8	27.39
0.24	1	2	69,540	48.7	23.12	0.24	1	2	63,560	44.5	26.25
0.16	2.8	10.7	65,640	45.9	25.67	0.16	2.8	10.7	56,947	39.8	28.94
Average of the Averages											

The above table shows 15.5 percent increased ultimate strength for Electric Steel and 11.3 percent decreased Elongation, as compared with Open Hearth Plate Steel of approximately the same chemical analysis.

A steel of greater density than our other commercial steels, with the possible exception of crucible.

In conclusion, let me say that the three electric furnaces of the Steel Corporation are the largest in the world that have as yet been put in operation. They have presented many interesting and complex problems, and the manufacturer has encountered occasional troubles. Although we feel that we are as yet but on the threshold of this method of manufacture, we feel that electric steel is a success and its future assured.

DISCUSSION

(New York City, April 8, 1911.)

MR. C. G. OSBORNE: The Electric-Bessemer process at the Illinois Steel Company is the same in its first stage, *i. e.*, during the blowing in the Bessemer converter, as in making rail-steel. The blown-metal is then transferred to the electric furnace, where something like 1950 kw. are used during the first half of the heat.

A MEMBER: Do you use cold scrap direct?

MR. OSBORNE: As a rule we use liquid material only. It is not an economical proposition to use cold material in any process if you have hot metal. It might interest some of the members to know that we have used the electric furnace for quite a number of heats of manganese steel, the furnace merely being used for melting ferro-manganese. Cold ferro-manganese is charged up to the capacity of the furnace and, when liquid, is tapped into a ladle and transferred to the open-hearth, and then added to a heat of open-hearth, the resultant mixture being manganese-steel. This is a new departure, I believe.

A MEMBER: How much manganese do you lose in so doing?

MR. OSBORNE: A very small percentage; sometimes as high as 3 percent.

A MEMBER: Will you give us a little information as to the cost of making electric steel?

MR. OSORNE: I cannot give you anything on that.

A MEMBER: What is the size of electrodes you are using?

MR. OSBORNE: Just at present we are using 14 in. (35 cm.) square carbon electrodes, manufactured by the National Carbon Company. We have tried every kind of electrode, however, and, for that matter, we are still using various kinds.

MR. L. E. SAUNDERS: Have you two of the same kind in use?

MR. OSBORNE: Yes, we have. We have used electrodes from 24 in. (60 cm.) diameter, round, down to 10¾ in. (27 cm.) square, some of which have been carbon and some graphite. The smaller sizes of electrodes, of course, are too small to carry the current, and for that reason get exceedingly hot.

MR. SAUNDERS: Have you any water-cooling arrangement at the electrode holders?

MR. OSBORNE: Yes, they are all water-cooled. These electrode holders are solid copper castings into which the cooling pipes have been cast. We also have an additional cooling device which we call an electrode-cooler. This consists merely of a hollow box arrangement around the electrode at the point where the electrode enters the roof. These cooling-boxes rest on the roof, and through them a constant stream of water flows.

PROF. J. W. RICHARDS: Have you tried to make a gas-tight joint there at the roof?

MR. OSBORNE: The cooling-box I have just spoken of serves to tighten this joint to some degree. In addition we have moveable plates which can be fitted closely around the electrode to form a satisfactory and tight joint. At Worcester this joint is absolutely tight, but at South Chicago during the first slag a great deal of ebullition of gas takes place, due to the addition of iron oxide. During this slag the bath "boils," and the electrodes are in constant motion up and down. During this period, it is difficult, on account of this motion of the electrodes and the large ebullition of gas, to keep a tight joint. During the second slag, however, the Worcester conditions are approximated and the joint can be kept efficient and tight.

MR. C. A. HANSEN: Has Mr. Osborne any analytical expla-

nation for the difference in hardness between open-hearth and electric steel?

MR. OSBORNE: I don't know what you mean by hardness. Do you mean the reason for the increased tensile strength in electric steel?

MR. HANSEN: Yes.

MR. OSBORNE: I do not think that the reason electric steel has unusual tensile strength is because of any difference in composition, because we have taken individual heats of electric steel for a year and a half, and compared them with open-hearth steel of almost identical chemical composition, and found the former to be the stronger. I believe this is on account of the greater density. I would say that 0.15 percent carbon, in electric steel, gives about the same tensile strength as basic open-hearth steel with 0.22 percent carbon.

MR. HANSEN: Will you give us some information as to the different results?

MR. OSBORNE: In the back of the paper there is a table showing the different averages of ultimate strength and percent elongation of electric plate-steel and basic open-hearth plate-steel.

MR. HANSEN: What do these heats run in manganese?

MR. OSBORNE: Ordinary plate-steel will vary from 0.30 percent to 0.60 percent manganese, with an average of about 0.40 percent.

MR. HANSEN: Do you use silicon for deoxidizing?

MR. OSBORNE: We do not as a rule deoxidize with silicon. Of course, all our steel is made to chemical limits which are specified by the customer. On rail steel, specifications call for about 0.1 percent to 0.2 percent silicon. To get this silicon we have to add ferro-silicon, about three-fourths of which is added in the furnace; therefore, in the furnace some of the deoxidation is undoubtedly due to this addition of silicon, which is made from ten to fifteen minutes before the heat is tapped. On ordinary basic steel, which does not call for the addition of silicon, we do not add it, and whatever deoxidation takes place is accomplished by means of a reducing slag.

MR. HANSEN: What percentage of free oxygen do you have in the steel?

MR. OSBORNE: We do not know; we have made several thousand experiments to discover that. We have had a man engaged constantly for two years on experiments to determine the amount of free oxygen in the steel, also the amount of nitrogen. We have also dealt with various other academic subjects of that character, but I do not think we have reached satisfactory conclusions.

PROF. S. A. TUCKER: Concerning the segregation in the ingot of manufactured product, what loss due to segregation have you found there is in the ingots compared with the open-hearth process?

MR. OSBORNE: Very much less. We make the claim that in electric steel, properly made, the segregation is practically *nil*, except in the portion immediately below the pipe; the rest of the ingot, and the portion around the pipe in the ingot, at each side of the cavity, is perfectly sound steel. This we have substantiated by a large number of tests.

PROF. TUCKER: Is that the explanation of the higher density of electric steel?

MR. OSBORNE: That, and the fact that it is freer from gas. The absence of gas in the steel as it is tapped will let the steel lie quiet in the mold, and permits all its particles to unite more closely.

A MEMBER: Has not someone shown that blown Bessemer material does not contain more nitrogen or oxygen than electric steel?

MR. OSBORNE: This would be certainly a very interesting statement. If blown Bessemer metal were poured into a mold 60 in. (150 cm.) high through a 1½-in. (3.7 cm.) nozzle, the metal would boil to such an extent that if the stream were shut off when the mold was apparently full, I do not believe you would have over two feet (60 cm.) of good metal in the mold when the steel solidified.

The question of how much oxygen is actually absorbed or dissolved in the solid metal is surely a different one from how

much gas is in solution in the liquid metal. If someone has found that blown Bessemer metal contains no more oxygen or nitrogen than electric steel, he refers undoubtedly to the gases found dissolved or absorbed in the solid steel.

Mr. Saunders: I would like to call attention to the fact that this is a fine example of what I consider to be a promising field for the electric furnace, *viz.*, to use it for taking care of the peak of the work of refining the steel; the larger part of the refining would be done by the gas-fired or coal-fired furnace, and only the most difficult part of it with the electric furnace. I consider that this offers a great future for the electric furnace, not only in the steel business, but elsewhere. One furnace that I have in mind is in use by the National Carbon Company, I believe, and is heated during the greater part of its run by gas, and only the last 300 or 400 degrees is supplied by the electric current. I think that is a very advantageous application of the electric furnace.

Prof. Richards: I think that the electric furnace may also very well be used simply as a dead melter in steel making, that is, make steel as good as you can make it in the Bessemer or open-hearth processes, and use the electric furnace simply to produce the equivalent of the dead-melt in the crucible. My proposition is to take otherwise finished steel from the Bessemer or open-hearth furnace, and hold it liquid, let us say thirty minutes, giving the oxides a chance to float up and the steel a chance to rest, thus giving it the equivalent of the dead-melt in the crucible. This will be a very inexpensive treatment, probably costing less than twenty-five cents a ton, where power is cheap, and not over fifty cents a ton at the most, and will produce results well worth the outlay.

Mr. Henry Hess: You stated a few moments ago that the melt came out of the electric furnace at about 190° less temperature than it went into the furnace?

Mr. Osborne: Between 100° and 120°, in high-carbon steels.

Mr. Hess: What advantage is there from the use of the electric furnace, except the one touched on by Prof. Richards, of allowing the steel to rest in the electric furnace?

MR. OSBORNE: Chemically, the steel is purified in both its phosphorus and sulphur contents. It is also freed from slag and occluded gases.

MR. HESS: You have a heat loss of 100° to 200° F. Is that refining necessarily attended with heat loss?

MR. OSBORNE: Of course, no heat loss is necessary. It would be possible to take cold scrap and make liquid steel from it. The fact that the blown metal sometimes enters the furnace at a higher temperature than that at which the steel is subsequently tapped is purely a question of operating conditions. The decarbonized and desiliconized metal has to be transferred in a ladle a distance of about a quarter of a mile from the Bessemer to the electric furnace plant, a proceeding which takes about ten minutes. With the delays that are likely to occur, it is necessary to have an initial temperature considerably above the solidifying point. This, and the fact that low-carbon steel has a higher solidifying point than high-carbon steel, accounts for the lower temperature at tapping than at charging.

PROF. RICHARDS: Several times the question of efficiency has been brought up, and I am sure that the question is not clear to some of us. There are two kinds of efficiency which can be recognized. One is present when you use the furnace as a melting apparatus, pure and simple, putting cold charges into the furnace and taking them out as soon as melted. The efficiency of that operation is the heat which you actually put into the material melted as compared with the heat energy of the electric current used.

There is another class of operation, in which you want to keep in a molten state, for further treatment, metal which has already been melted. In that case there is no such thing as the first kind of efficiency in question. The efficiency in this case can only be expressed in terms of the rate of supply of energy which you use to keep a certain weight of metal melted, at a given temperature. One furnace will keep a ton of steel melted with 50 kw., another uses 100 kw., and still another furnace will require 200 kw. or more. This is the basis upon which you must compare the efficiencies of electric furnaces which simply keep metal melted while it is being treated.

In many operations you have the two efficiencies combined; first of all, the operation of melting the metal, and when you have it melted and at the desired temperature, the heating is continued while the metal is being treated; the two efficiencies in this case are, first, the melting efficiency; and, second, the power requirement to keep the metal melted at the desired temperature, or, properly speaking, the reciprocal of the latter.

Mr. F. A. Lidbury: Then it seems to me, Mr. President, that Prof. Richards has clearly shown that nothing at all is to be gained by referring in any case to the "thermal efficiency" of an electric furnace. As he has clearly stated, in many cases the term has no meaning whatever. I do not think that anything is to be gained by setting up terms of which the meaning is so far from general that a different definition practically has to be adopted in every different case, and I think that our discussions of the thermal side of the electric furnace practice would be very much simplified if this term were dropped altogether.

Prof. Richards: I do not agree at all with Mr. Lidbury. I believe that we can distinctly and usefully distinguish these two stages: First, the heat-giving stage, or the melting stage; secondly, the stage where you simply keep the melted metal in the molten state. The first is conformable to the usual definition of thermal efficiency, in the common acceptation of that term, and the second stage, which involves the amount of power necessary to keep the metal melted, is an entirely different kind of efficiency. I hope our electric furnace operators will keep these two ideas distinct and will designate the running efficiency of electric furnaces on the basis of the amount of power required to keep a ton of steel melted. There are some furnaces which require 250 kw. to keep a ton of steel melted, and there are other furnaces which require only 50 kw., and one furnace is, therefore, five times as economical in practice as the other. Mr. Osborne's furnace consumes 750 kw., simply to keep 15 tons of steel at a proper temperature for treatment. That is 50 kw. per ton of steel kept melted in the furnace. You can compare all electric furnaces used in this way on that basis, and it will tell you their efficiency with reference to radiation and keeping the charge melted.

Another kind of efficiency is in question when you put cold material in the furnace and raise its temperature; in that case you have an efficiency equal to the ratio of the amount of heat going into the steel to the heat equivalent of the electric energy used. When you have it melted and at the desired temperature, the first kind of efficiency disappears and the other efficiency comes in. If you put metal into a furnace melted, the first efficiency also does not come in. The two kinds of efficiency rest on a different basis; they are both useful things to know, and I hope our electric furnace people will work them out in detail and keep them constantly in view, because they give valuable information.

MR. LIDBURY: I shall be glad to continue this discussion with Prof. Richards under circumstances that will enable it to be more perfectly threshed out than the time now at our disposal will permit.

I will point out that in his concluding remarks he has accepted the point of view that I have adopted. He has said nothing about the percentage efficiency of the South Chicago furnace. He stated that a certain quantity of energy was consumed per ton of steel. That is the kind of statement about a furnace that means something. To say that it has a certain percent thermal efficiency does not mean anything.

DR. I. LANGMUIR: Is it not merely a question of words? The thermal efficiency in the first sentence is "efficiency" in the ordinary sense of the word. When we speak of efficiency, we ought to be able to conceive of something that is 100 percent efficient. A furnace of the first kind might approach 100 percent efficiency as a limit. The use of the word "efficiency" in the second sentence is what causes the confusion. Can we not find some other name for the condition we wish to describe than "efficiency"? To call it "efficiency" is misleading, because it is inconceivable how a thing of that kind can be compared with 100 percent efficiency. It cannot be expressed in percentages at all. It simply means the heat required per ton per hour. Now that is a quantity which is of great value in comparing different furnaces, but it is not "efficiency," since it does not approach 100 percent as the furnace becomes more nearly perfect,

but actually approaches zero in the case of the most efficient furnaces.

PROF. RICHARDS: It is "comparative efficiency."

DR. LANGMUIR: That would be some improvement, but we had better have another word for it. If someone could think of a suitable word to use in place of "efficiency," I am sure there would be no further objections. The heat required per ton per hour is really "specific power consumption." If a single word is wanted in place of this phrase, perhaps the word "wattivity" would prove useful after its novelty wore off.

MR. A. L. QUENEAU: Do you run the furnace seven days a week?

MR. OSBORNE: No.

MR. QUENEAU: How do you make your furnace hot and bring it to working condition?

MR. OSBORNE: We have two methods. We heat it with oil burners, or put coke on the bottom and lower the electrodes on the coke till it is incandescent.

MR. QUENEAU: How many watts do you need to keep it hot over shut-downs?

MR. OSBORNE: It depends on how long the furnace is out of commission.

MR. QUENEAU: Twenty-four hours, thirty-six hours or forty-eight hours?

MR. OSBORNE: It is a difficult question to answer. You ask something that does not mean anything. If we shut down for thirty hours, we let the furnace get comparatively cold and then start to heat again. If we shut down for six hours, we keep the furnace hot all the time. We do not have any regular practice in that matter.

MR. QUENEAU: How cold do you let the furnace get?

MR. OSBORNE: As cold as it wants to, in thirty hours. If we do not get any orders, we may shut down for four or five days. In that case we start with oil and finish the heating of the furnace with coke. The furnace should be hot before it is used. If

you put hot metal into it before it is heated, it will destroy the bottom of the furnace.

MR. T. F. BAILY: What figure do you take for the specific heat of your molten steel?

MR. OSBORNE: I never used that. I do not know.

DR. LANGMUIR: There is surely some advantage in knowing the specific power consumption of different furnaces. The furnaces you have are probably of better or worse design than some furnaces in other plants. To be able to compare them is useful. One of the factors in such a comparison is certainly the relative power required per ton of metal under similar conditions.

MR. HIBBARD: I notice that Mr. Osborne said he used 1,950 kw. in his furnace, and he admitted to Mr. Richards that 750 kw. would keep the charge melted. What is the reason for the discrepancy?

MR. OSBORNE: When we start a heat of steel in the South Chicago electric furnace, we drive the current into the steel as fast as we can get it, up to 1,950 kw., about 650 on each leg. This is necessary and the quickest manner in which we can liquefy the slag. Towards the end of the melt, however, when the reactions have taken place, much less power is required to maintain the temperature. That is the reason for the apparent discrepancy in the two statements.

MR. CARL HERING (*Communicated*): Concerning this much abused term "efficiency," it is in my opinion a mistake to limit it, as some do, only to such relations as would become unity or 100 percent in the case of a theoretically perfect efficiency, that is, to the quotient of two quantities which are physically the same, but differ merely in quantity, as for instance energy divided by energy. It is true that then only can efficiency be represented in terms of a percent. There is no lack of precedent for the use of the term efficiency when the two quantities are not physically the same; hence if common and usual practice justifies usage, it is not improper to use the term efficiency in such a sense also. As illustrations, we have the common and very useful expressions: candles per watt, lamps per horsepower, pounds of coal per horsepower-hour, pounds of steam per pound

of coal, pounds of steam per square foot of heating surface, pounds of coal per car-mile, etc., all of which are efficiencies, or the reciprocal, inefficiencies. Hence it would not be contrary to well-established practice to refer to the kilowatts per ton to keep iron melted in a furnace, or the kilowatt-hours per ton to refine steel, as true efficiencies of a furnace.

Mr. Osborne (*Communicated*): In connection with the discussion of thermal and heating efficiencies, I would like to point out that the electric furnace at South Chicago has quite a little melting of cold stock to be performed, in the way of iron ore, manganese ore, lime, fluorspar, etc. And also that it frequently happens that, due to unavoidable operative delays, the furnace bottom, between the tapping of one heat and the charging of another, cools down to such an extent that, on charging the next heat, the liquid blown metal solidifies in certain places. When this happens, the skull which has formed must, of course, be re-heated to a molten condition.

A paper read at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, Saturday, April 8, 1911, President Wm. H. Walker in the Chair.

ELECTRIC STEEL PROCESSES AS COMPETITORS OF THE BESSEMER AND OPEN HEARTH.

By Albert E. Greene.

Electric furnace processes in steel manufacture have heretofore been used largely for the production of high grade steel, and have not been considered competitors of the Bessemer and open-hearth processes for making ordinary grades of steel. The object of this paper is to discuss certain characteristics of the processes commonly employed for making ordinary steel, and thus to lead up to the consideration of a new electric furnace process which, by reason of improved economy of metal, bids fair to take a place of prominence in the development of a successful competitor to the Bessemer and open-hearth processes. The characteristics of these old processes to which attention is particularly called are the unavoidable losses of metal incident to such steel processes and the chemical reactions responsible for the great losses that occur.

In the Bessemer process alone in the United States, the loss of metal by undesired oxidation, vaporization, etc., amounts according to some authorities, to half a million tons per annum, assuming a total production of ten million tons of Bessemer steel. In the acid Bessemer process as practised at many places in the United States the decrease in weight of the charge during the conversion process is at least 10 percent of the weight of the pig iron charged; about one-half of this decrease in weight results from the elimination of carbon and silicon, the remaining one-half is a sheer loss of metal. In short, in the conversion of pig iron into steel by the Bessemer process there is a loss of iron, which is so much waste, which approximates 4 or 4.5 percent of the total weight of the charge, and practically all the manganese, which latter approximates 0.5 percent, making a total unavoidable loss of about 5 percent of the weight of the charge in these two

metals. Harbord gives the yield of metal in the *acid* Bessemer process as 86 to 88 tons of ingots per 100 tons of metal used, and in the *basic* Bessemer only 83 tons of ingots. In the operation of small side-blown converters the decrease in weight during the conversion process often averages over 18 percent, and the greater loss is due to the increased length of blow which gives the oxygen more opportunity to oxidize the metal. In the basic Bessemer process, even in large vessels, the loss in weight is also very high,—according to some authorities 15 percent; and the basic open-hearth, although considerably better in this respect, is itself open to the same criticism. A somewhat misleading fact in connection with the open hearth process is that the yield is often based on the weight of metal charged without taking account of the ore used which remains unreduced in the slag. One sometimes hears of open-hearth furnaces with an efficiency of over 100 percent. Some authorities give the amount of iron lost in the open-hearth slag as 2.5 percent of the weight of steel made, and the loss of manganese as 0.5 percent. For the sixteen million tons of open-hearth steel made per annum in this country this loss of both iron and manganese would amount to 480,000 tons, and the total loss of metal from all processes would approximate one million tons per year.

It is well known that at the initial temperature of the Bessemer blow, 1200° to 1300°C., the oxygen of the air blast attacks the silicon of the charge more strongly than it does the iron or the carbon. This oxidation of silicon produces a large amount of heat, sufficient to raise the temperature of the bath of iron several hundred degrees, at which latter temperature the affinity of oxygen for carbon becomes greater than its affinity for silicon. This relative change of affinities of silicon and carbon takes place at a certain definite temperature, probably about 1425°C. After the carbon is eliminated the metal is poured into a ladle and spiegeleisen, containing about 15 percent of manganese and about 4.5 percent of carbon, is added. This addition serves two purposes; it deoxidizes the steel, since a portion of the manganese in the spiegeleisen unites with the oxygen in the metal and rises as a slag; and second, it brings the composition of the steel up to specification in manganese and carbon.

The basic Bessemer process differs from the acid process in

that the former eliminates phosphorus whereas the latter does not. In the basic Bessemer process the phosphorus is the last of the impurities to be oxidized and the operation is carried out in a basic lined vessel, and with the use of a lime slag to aid in holding the oxidized phosphorus.

In the several modifications of the Bessemer and also in the open-hearth process it is noticed that the different impurities show different tendencies to oxidize under different conditions. Silicon is usually the first element to oxidize and manganese has about the same tendency. The affinities of different elements for oxygen vary with the temperature; as the temperature rises above what is called the critical temperature for silicon and carbon the relative tendency of the two elements to oxidize is reversed and the carbon has preference. The point of temperature at which this change occurs may be readily ascertained in the operation of the Bessemer process by the appearance of the carbon flame. At high temperatures the affinity of phosphorus for oxygen is less than that of carbon and greater than that of iron, but we find that the relative affinity of phosphorus for oxygen varies very considerably also.

In the Monell and similar processes, in which the phosphorus is oxidized out at pig-iron melting temperatures, the phosphorus has at such temperatures a greater affinity for oxygen than either carbon or iron and under such conditions oxidizes out first. It is a fact, however, that in the practice of the Bessemer and open-hearth processes in their various modifications more or less of all the elements are oxidized, although some one element usually has a marked preference for the oxygen. It has been suggested, as a theory to explain this preferential action of the oxygen on some one element, that while several elements are oxidized, the one having the greatest affinity for oxygen robs the others of most of the oxygen they may have taken up. It is evident at least, that the different elements present in pig iron have quite different tendencies to oxidize at different temperatures and that the preferential oxidation may be more or less controlled in the ordinary processes by controlling the temperature. Thus, if we desire to oxidize silicon first, it is necessary to keep the temperature low, probably below 1425°C. (I give this particular temperature from results of my own experiments, never

having seen it published.) Numerous means have been proposed to do this, such as the use of carbon dioxide as the oxidizing agent, since carbon dioxide takes up a large amount of heat in splitting up and thereby cools the bath. But the use of such an agent does not prevent the partial loss of the alloying metals, since the carbon dioxide is an oxidizing agent with respect to both the carbon and the other elements present. If it is desired to oxidize carbon first from a bath of pig iron it is necessary to maintain the temperature above the critical temperature and it was proposed early in the history of electric furnaces to do this in an electric furnace and simultaneously blow the bath with some oxidizing agent. It was even proposed to use gases containing carbon dioxide in an induction electric furnace early in the 90's, to refine iron.

It was also proposed at an early date in the history of the Bessemer process to take advantage of the critical temperature above mentioned for the purpose of retaining alloy metals, such as manganese and silicon, in the metal during the elimination of carbon. In Germany a process was practised in Bessemer converters which consisted in using a high manganese iron, containing as much as 5 percent of manganese, the temperature rising fast enough, due to the oxidation of part of this manganese, so that the critical temperature was reached before all the manganese had been oxidized. In this way steel was made in which some of the original manganese was retained, but the product was not found satisfactory. The resulting steel is said to have contained blow holes and to have been brittle, and largely for these reasons the process is not practised to any extent.

It is a most interesting fact that much of our iron ore contains the elements manganese and silicon in sufficient quantity to meet the specifications of ordinary steel, and moreover, these elements are reduced in the blast furnace and are almost invariably present in the pig iron in sufficient quantity to meet such requirements without any additions, were it possible to save them in the converter. But during the converter blow the silicon and manganese are practically all eliminated, and then these alloying metals are put back again by charging some expensive alloy additions into the steel. It costs to reduce these elements in the blast furnace, in coke, labor, etc., and it costs to replace

them again after they are oxidized. The value of the manganese so lost is quite important. If the nine million tons of Bessemer steel produced in this country last year was made from iron containing 0.5 percent or more of manganese, 0.4 percent of which was lost in conversion, the total weight of metallic manganese so lost would have amounted to 36,000 tons; and if the specification required 0.5 percent manganese and 0.1 percent had remained in the iron, there would have been added to the blown steel enough spiegeleisen to give this. It would have required more than 225,000 tons of spiegel containing 16 percent manganese, assuming no loss in making the addition; but there is a loss of manganese which probably exceeds 25 percent of that retained. The total loss of manganese including this 25 percent loss would have been 45,000 tons. The actual total loss for both Bessemer and open-hearth processes is probably far in excess of this. Now if this wasteful oxidation can be prevented, it will not only make the costly additions unnecessary, but more steel will result from the same quantity of pig iron. There is undoubtedly a chance here to apply the principles of conservation to our metal industry.

The open-hearth process is not essentially different from the Bessemer so far as these chemical reactions and losses are concerned, although the losses are less, but in the basic open-hearth process the presence of iron oxide is considered essential to the elimination and holding of the phosphorus out of the metal and this oxidation is a material loss.

I wish to point out in this paper how the electric furnace, in combination with a control of chemical reactions by regulating the gaseous agents, provides a means of producing metal of higher grade and of doing it more efficiently and with far less loss than is possible in Bessemer or in open-hearth furnaces, and to describe a new process which takes advantage of a combined control of temperature and gaseous reagents to accomplish such a saving. The chief advantage of the electric furnace does not consist simply in its ability to produce extremely high temperatures, but rather in the fact that it provides a means of maintaining a charge at any given temperature, thereby enabling one to control the composition of the atmosphere at will. This control enables us to accomplish hitherto unthought-of results. In

this connection it will be of interest to consider for a moment the meaning of the term "neutral" as commonly applied to the atmosphere within furnaces in general, including electric furnaces. "Neutral" means inactive. But the atmosphere, if of proper composition, may react in such a way as to greatly aid a metallurgical process; for instance, the atmosphere in a steel producing furnace might be reducing toward iron oxide and prevent the steel from oxidizing; or it might be oxidizing toward carbon or phosphorus and thereby eliminate them. Now, it is a most interesting fact that we can have an atmosphere which is reducing with respect to iron oxide and nevertheless oxidizing toward carbon or toward phosphorus. For this reason it seems to me that the term "neutral" and also the term "non-oxidizing" is very indefinite, where there are different elements present, unless it is stated with respect to what the atmosphere is neutral or non-oxidizing.

I have just made the statement that it is possible to have an atmosphere which simultaneously is reducing toward iron oxide and oxidizing toward carbon. The principle underlying that fact is the basis of a new process for oxidizing carbon out of iron without oxidizing the metal itself. The conditions under which such reactions might theoretically be carried out are well worth considering. If molten pig iron be placed in a closed crucible, made of magnesite for instance, and kept at a uniform high temperature, and the space above the iron in the closed crucible filled with CO_2 gas, the gas and iron will react and finally come to a state of equilibrium. The reaction might be represented as follows:

$$CO_2 + Fe = FeO + CO$$

Under the equilibrium conditions which would be reached the ratio of the amounts of the two gases present would have a given value for the particular temperature. If we then replace the mixture of these two gases by another mixture containing relatively more CO and less CO_2 than the equilibrium mixture, and allow this new mixture to react with the iron and the iron oxide, some of the FeO would be reduced and the CO_2 component of the gas increased. This replacement could be made continuous by successive introductions of the new mixture. In this way

reduction of iron oxide could be carried practically to completion, and moreover, this could be done by means of a gas containing an oxidizing agent for carbon.

This was the theory on which the American Electric Smelting and Engineering Company started in its experiments several years ago to develop a practical process for converting pig iron into steel and refining it without oxidizing the iron and other valuable constituent metals. An extensive series of experiments has been carried out. The first experiments were made in small, electrically heated, magnesite crucibles holding only a few pounds at a charge. Pig iron and various other metals were treated at different temperatures with various mixtures of oxidizing and reducing gases for the purpose of ascertaining what ratio of reducing gas must be present to prevent oxidation. Almost pure CO_2 gas was used in some instances, and CO gas in others, and then various mixtures of such gases. It was found that a wide range of composition would still accomplish the desired results. There is, of course, a limiting value for the amount of oxidizing agent required as well as of the reducing component; exclusively reducing gas accomplishes no oxidation, and exclusively oxidizing gas not only accomplishes no reduction, but on the contrary oxidizes more or less of all the elements present.

Professor S. A. Tucker, of Columbia University, was kind enough to extend to me the privilege of making some of the tests in his laboratories, from which valuable data were obtained.

It was found that producer gas might easily be made to serve the purpose, and that a producer gas containing as little as 4 percent of CO and as much as 15 percent of CO_2 would, when blown into molten pig iron at a temperature of about 1450°C. eliminate the carbon with practically no oxidation of iron, manganese or silicon.

After carrying out a series of tests in these small electrically-heated crucibles, and finding it practical to separate different elements such as carbon, phosphorus and silicon from iron without material loss of the other elements which it was desirable to retain, we employed an induction furnace of about 300 pounds (136 kg.) capacity to test the process on a practical scale.

This furnace had an enlarged portion at the back, forming a pot, and tuyeres were put into this part in much the same way

as they are put in a Tropenas converter. The photographs show this small furnace, and also the gas producer, and electrical apparatus used in connection with it.

The process consists in providing a bath of molten low-phosphorus pig iron containing, for example, the usual proportion of manganese, silicon and carbon, leaving out of the question for the moment the removal of phosphorus and sulphur which I will take up later. The charge preferably contains sufficient manganese and silicon to slightly more than meet the specification for the particular steel to be made. The temperature of the bath

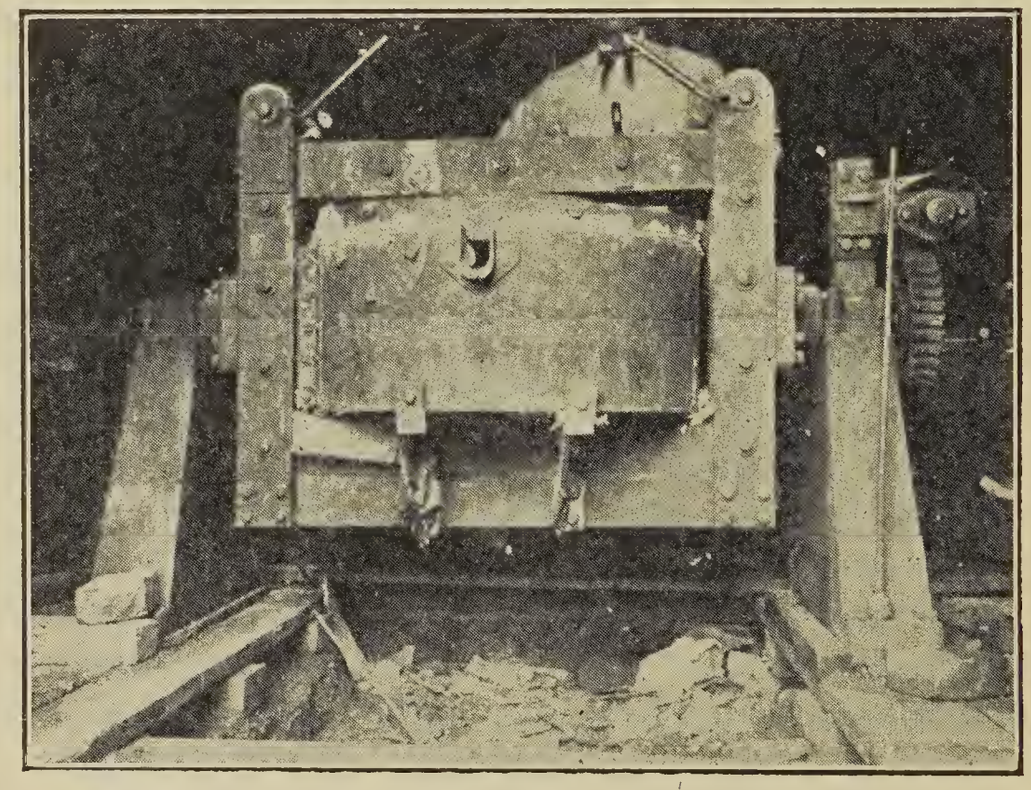


Fig. 1. Inductor Electric Converter.

is raised to something over 1425°C. which is maintained by the electric heating, while a gaseous mixture containing CO and CO_2 is blown into the metal in much the same way as air is blown into a Tropenas converter. This mixture may contain 12 to 18 percent of CO_2 and 5 percent or more of CO.

The rate of elimination is a little slower than with the Bessemer process for the same rate of blowing. A well-operated side-blown converter requires from 25 to 35 minutes to make a blow, using about 1,500 cubic feet (43 cub. meters) of air per minute per ton of metal. In this small induction furnace, using about 50 cubic

feet (14.3 c.m.) of gas per minute per 200 pounds (91 kg.) or about one-third the rate of blowing in the side-blown Bessemer vessel just referred to, the carbon can be eliminated in something more than an hour and one-half, depending on how much carbon there is at the start. Thus, with only one-third as much gas blown per minute per unit weight of metal, the time is a little more than three times as long as for a similarly blown vessel using air. By increasing the rate of blowing the time can be very greatly cut down. We carried out tests to determine the minimum time under the best conditions of contact of gas and metal we could maintain, and found that it was possible to eliminate the carbon in 18 minutes without oxidation of the metal. The rate of elimination depends largely on the nature of the contact of the gas with the metal, and when the gas is blown through the metal it is most rapid.

It was found that the gas could be blown into the metal without any formation of slag on the surface of the metal and without any boiling. If an oxide slag had formed before the blow, as might happen when rusty scrap is melted to make up the charge, we found it possible to practically completely reduce this iron oxide during the blow simultaneously with the removal of carbon. In this small furnace pig iron can be converted into steel with as small a loss of iron, manganese and silicon as 2.5 percent, including losses in charging and spills in handling the steel. In view of the difficulty of handling molten steel in such small quantities as only 200 pounds (91 kg.) without losing a few pounds this loss seems extremely low. In small Bessemer vessels holding as little as 300 pounds (136 kg.) the loss of metal is said to be not less than 20 percent, aside from the loss of weight by oxidation of carbon.

The most convincing evidence that oxidation does not take place in the process may be found in connection with the loss of manganese. In converting a 13.4 percent spiegel into manganese steel, we have done this without any additions of any kind, and have produced a steel containing over 12.5 percent manganese, and this was without the use of a slag to prevent vaporization. The carbon was reduced from over 4 percent to 1.20 percent. In later tests, using a lime slag, the vaporization loss has been further diminished.

It is well known that the high percentage of carbon present in commercial ferro-manganese makes it practically impossible to obtain as much as 12 to 14 percent of manganese in manganese steel without raising the carbon content above 0.9 or 1 percent. No great difficulty is met with in producing very low-carbon manganese steel by the process described in this paper; and the properties of low carbon manganese steels are very interesting.

With regard to the quality of steel made the objection has

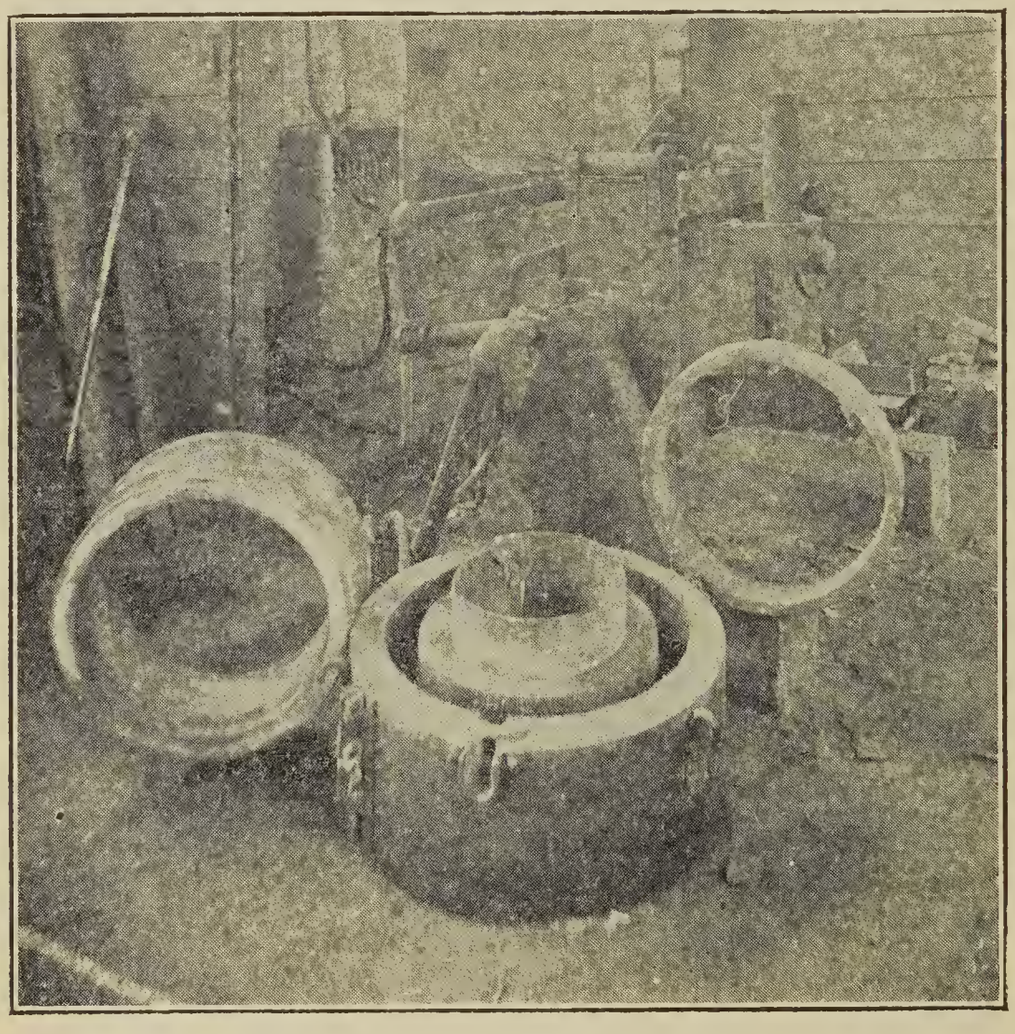


FIG. 2. Parts of Induction Converter.

been raised by steel makers that steel made without additions and by retaining part of the original content of such elements as manganese and silicon, will not be sound; but we have demonstrated that in this process the metal can be made absolutely sound and free from blow holes and of as good quality as other electric furnace steel.

Reference has already been made to the conversion of spiegeleisen into manganese steel. The process can be very usefully

applied also to making manganese steel from pig iron and manganese steel scrap. In carrying out this application of the process molten pig iron is charged into the converter and the scrap is melted into the molten iron, meanwhile keeping a small amount of gas passing through the furnace which prevents oxidation of manganese and aids decarbonizing. After melting the scrap into the molten iron the temperature is raised to about 1450°C. and kept there and meanwhile the bath is blown with the gas already referred to. The percentage of carbon may be regulated by stopping the blow when enough has been taken out, and in case it is desirable to remove silicon this may be done by charging a lime slag on the bath. Of course where the charge consists in part of iron or steel low in manganese, ferro-manganese is added to raise the manganese to the desired percentage. After the composition is attained the temperature is regulated and the metal poured. The power consumption for melting manganese steel scrap into molten pig iron need not be more than 500 kw.-hours per ton, and at a cost of 1 cent per kw.-hour, the power cost would not amount to more than $5.00 per ton. The value of the manganese which can be saved is considerably in excess of this.

Such application of the process as just described is suitable for utilizing any kind of alloy steel scrap such as armour plate and tool steel scrap, not only cutting down losses and additions but producing a higher grade of product.

Let us next consider the application of the process to the removal of phosphorus and sulphur and to the production of a high-grade steel from low-grade pig iron in one continuous process; and for the sake of comparison let us consider the basic open-hearth and basic Bessemer process for removing these elements. The chemistry of these processes is not altogether clear. Lime is necessary to hold the phosphorus out of iron after it has been oxidized and the presence of iron oxide has been considered more or less essential. In the open-hearth process, and also in the electric process, the iron oxide is present as ore or scale; in the basic Bessemer it is formed by the action of the air on the iron and this is supposed to combine with the phosphorus. Thus the phosphorus is held in the slag as an iron-calcium-phosphate. Another interesting fact about phosphorus is that it can be oxidized either before carbon or after carbon. If the tempera-

ture of the iron is low, say about 1300°C. phosphorus may be oxidized very rapidly and with very little oxidation of carbon. This action usually takes place after the silicon has been nearly all oxidized; on the other hand, in the basic Bessemer converter

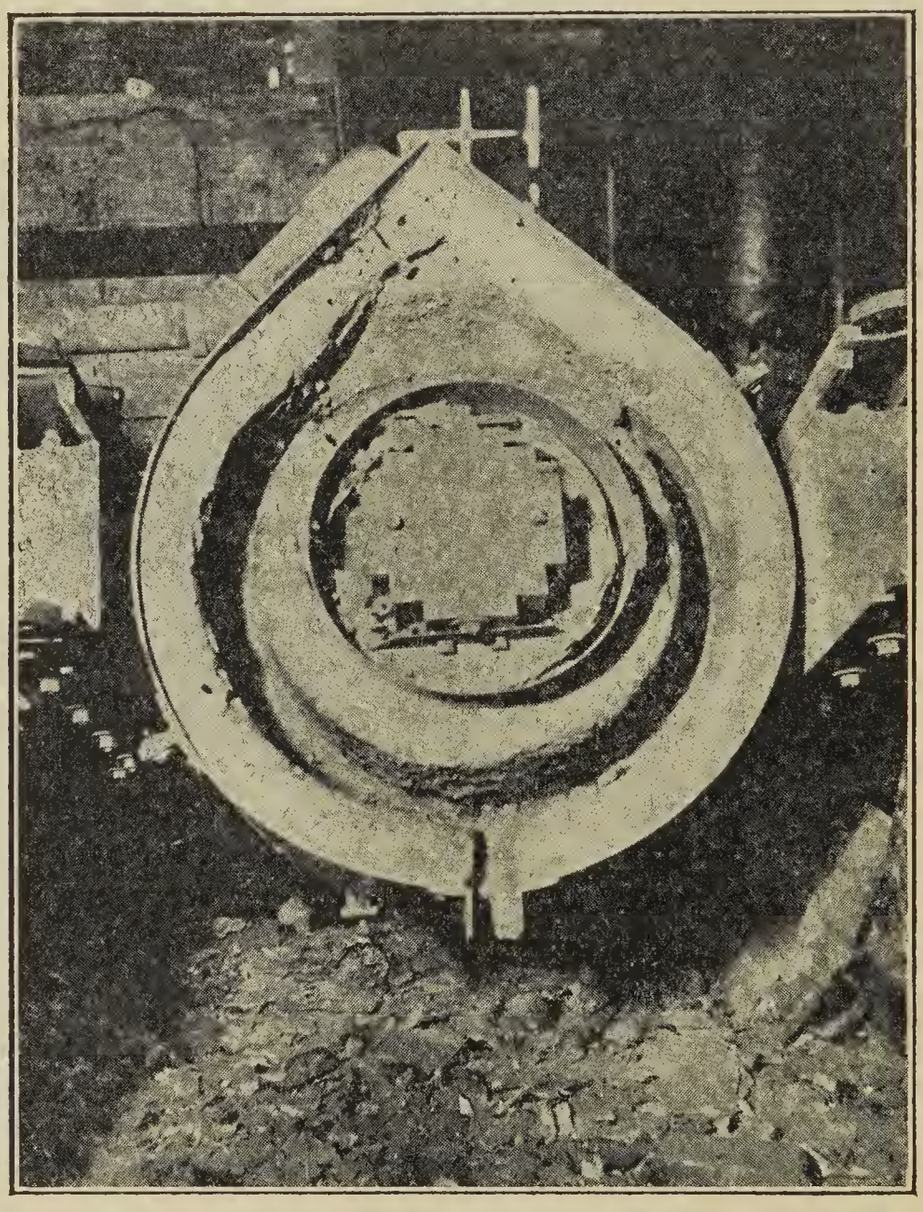


FIG. 3. Induction Converter, Cover Removed.

phosphorus is the last thing to oxidize and does so only at high temperature.

The slags of both basic open-hearth and basic Bessemer processes contain rather large percentages of iron as well as practically all the manganese and silicon originally in the iron and it is this feature, namely, the necessity of having iron oxide present that causes the greater loss by oxidation in basic processes than in acid processes.

We further find in the operation of these processes that sulphur is difficult to separate from the metal when there is a large amount of iron oxide present in the slag and so very little is removed in either the Bessemer or open-hearth. In the Heroult process, the basic slag used to take up phosphorus must be removed, and a lime slag added, together with coke or other agent, before the sulphur is materially taken out. Leaving out of the question the electric furnace, the present Bessemer and open-hearth processes are therefore practically limited to reasonably low-sulphur iron.

The process described above for oxidizing carbon without oxidizing iron is similarly applicable to the removal of phosphorus. We have found that we can oxidize phosphorus out of iron and hold it out by means of lime and do this with practically no oxidation of iron and manganese. We have done this at pig iron melting temperatures below 1350°C. without oxidizing carbon, and we have done it at high temperatures, above 1500° C. and up to 1900°C. after carbon has been oxidized. And beside these facts we found that the sulphur can be taken up and held in this same slag that holds the phosphorus, which action we attribute to the absence of oxide of iron in the slag.

We have converted a low-grade pig iron into a high-quality steel in one continuous operation in this way, taking out the carbon without oxidation of iron and manganese and then, with a lime slag on top of the metal, by continuing the blow of the gaseous mixture, the phosphorus has been oxidized and eliminated. The phosphorus was found combined with the lime as calcium-phosphate and practically all the sulphur was found in the slag as calcium-sulphide.

We have had such results as follows:

Analysis of charge.....Phosphorus 0.76 %. Sulphur 0.113%
Analysis after blow.....Phosphorus 0.026%. Sulphur 0.040%

Analysis of charge.....Phosphorus 0.094%. Sulphur 0.040%
Analysis after blow.....Phosphorus 0.008%. Sulphur 0.017%

We have carried out such a conversion of molten pig iron into refined molten steel as just outlined in less than 30 minutes, which indicates that the reaction takes place quite rapidly and that the

problem of installing the process in large vessels of ten or more tons capacity is a mechanical one of getting the gas into the metal.

It may be of interest to compare the operation of making steel castings in a small plant using a side blown Bessemer converter and in one fitted with an electric converter using the process described in this paper.

In the Bessemer plant, molten, low-phosphorus pig iron is poured into the converter and blown until the carbon is practically out. The vessel is acid-lined and no phosphorus or sulphur can be removed, so that the highest quality of iron must be used. This grade of iron usually contains about 2 percent of silicon and 0.5 to 1 percent of manganese. As already stated the total loss of weight during the conversion often averages 18 percent and as much as 12 or 13 percent of metallic iron may be oxidized. In a small plant recarbonizing and deoxidizing is usually done by adding ferro-manganese and ferro-silicon in the ladle and even in this part of the process there is a further loss due to the oxidation of these alloys in entering the steel.

To get some idea of the value of the metal lost by oxidation, consider a small plant making, say 20 tons of castings per day from 32 tons of molten steel and converting about 39 tons of molten pig iron per day to make the 32 tons of molten steel. Of the 7 tons loss, about 5 tons is metallic iron. The loss per year of 300 days would be 1,500 tons. If this metal had been saved as steel its value, at $30,00 per ton, would be $45,000. Such a loss is clear waste. Besides the iron there are other losses. Suppose the specifications requires 0.60 percent of manganese; the cost of the 80 percent ferro-manganese required to give 0.60 percent manganese in the steel might easily be 45 cents per ton of steel or $4,320 per year. Practically one-third of the weight of ferro-manganese in the steel is lost in slag.

If it is possible to eliminate carbon without eliminating manganese it would be very simple to use a pig iron containing sufficient manganese to meet final steel specifications and not only would it be possible to dispense with the ferro-manganese additions costing about 45 cents per ton of steel, but the 0.60 percent of manganese saved would mean 0.6 percent more steel from the same weight of pig iron. It is by the saving of such metal

that we believe the increased cost of the electric-converter process will be much more than justified but in this connection one or two of the items of cost in the electric converter process will be discussed later in this paper.

Before leaving the small Bessemer plant there are other facts to be considered, especially those relating to the phosphorus and sulphur. There is a very considerable difference in the price of low-phosphorus iron and Bessemer iron. If Bessemer iron containing, say 0.09 percent of phosphorus could be used instead of iron containing less than 0.04 percent of phosphorus there would be a saving of several dollars per ton over the higher grade iron; if still lower grades of iron, containing more phosphorus, could be used, the difference in cost would be much more marked. As is well known, it has been proposed to combine some form of electric furnace with an acid-lined converter and, after blowing the metal in the converter and eliminating silicon and carbon, to transfer it to the arc furnace and there dephosphorize, desulphurize and deoxidize it. Such a combination process using an arc furnace, the Heroult or the Girod furnace for example, has important advantages, especially in respect to the quality of steel which it is possible to produce. It is the opinion of some well-known steel men however, that such a combination is not adapted to the refining of high phosphorus and high sulphur iron and that the cheapest method of refining such low-grade iron is in the open-hearth, finally giving the refined steel a finishing treatment in an electric furnace.

Probably one reason for this opinion is that electric furnace refining requires two distinct slagging operations; the first, an oxidizing slag similar to a basic open-hearth slag; and the second, a reducing or deoxidizing slag replacing the first one. The action of the first one differs little if any from a basic open-hearth slag; it is hotter and therefore possibly more rapid in its action, but this advantage is offset by the high electrode and power cost. Yet in the electric process for removing phosphorus and sulphur as practised to-day it is not practical to eliminate these impurities and also deoxidize the steel with only a single slag.

There are other disadvantages resulting from transfering blown steel to an electric furnace to eliminate phosphorus, namely, the loss of heat and time by such transfer, the additional labor and

expense involved, and the cost of reheating the metal after it is in the electric furnace. My point is, not that such a method is not advantageous, but rather that it has certain disadvantages which are avoidable.

This leads me to the consideration of the electric converter process by which it is proposed to avoid these difficulties.

This electric converter process may be compared with the Bessemer process from two standpoints; first, assuming that only low phosphorus and low sulphur pig iron is used; and second, assuming that impure iron is used. The program of the electric converter process for treating low phosphorus and low sulphur iron would be as follows: The molten pig iron is charged into a basic lined electric converter. The type of converter which has most advantages for this purpose is an induction furnace having a main central hearth into the back side of which the tuyeres enter, and having two or more induction channels connecting with this main hearth.

The pig iron ordinarily would contain 1.5 percent of silicon and 0.75 percent to 0.85 percent of manganese. If low silicon iron could be readily had it would be so much the better for this process. But high silicon iron, which is more common, may be worked by the process, it merely involving the additional steps of lowering the content of silicon. Lime or limestone may be used for this purpose and is charged into the molten iron at the start. The metal, heated to about 1450°C. is blown with a gaseous mixture which might well contain about 8 percent CO and 15 percent CO_2. The carbon is taken out until a fracture sample shows that the proper carbon remains. It is possible, by timing the blow to come very close to the desired percentage of carbon. The loss of manganese will be small enough so that the final percentage should not differ more than 0.05 or 0.10 percent from the percent at the start. The silicon may be entirely removed or only in part. Finally any killing treatment desired may be given to the steel after the desired analysis is attained. In this process the oxidation loss of iron and manganese common in Bessemer practise can be almost entirely avoided.

The operation when high phosphorus and sulphur iron is used is quite similar to that just described. The raw material of course consists of low grade iron. It is charged molten into the

electric converter and lime is added to take up and hold the phosphorus and sulphur. In one method of operation the blow of gas is continued until practically all the carbon is oxidized and eliminated, a few tenths of one percent only remaining, and likewise until the silicon is practically all taken up by the lime, as calcium silicate. Continuation of this blow in the presence of the lime slag then takes out the phosphorus without formation of iron oxide. The interesting feature is that sulphur is also taken out and held out of the metal by that same slag. By this treatment the heavy loss of iron in the basic slag common to basic processes is avoided, and at the same time the slag is enabled to take up sulphur, which is in marked contrast with the basic process wherein the presence of iron oxide in the basic slag prevents such removal of sulphur to any great extent.

Instead of practising this process as just oulined it is possible to apply it to molten pig iron at relatively low temperature and take out both phosphorus and sulphur *before* carbon. Contrary to some statements to the effect that a high temperature is necessary to remove sulphur, it was found in the tests we made that sulphur could be rapidly removed from molten pig iron at temperatures as low as 1200° to 1300°C. by the action of the gas together with a lime slag to which was added a small amount of fluorspar to increase fluidity. The sulphur was usually found in the slag as calcium sulphide.

As compared with the combination process using a Bessemer converter and an electric furnace, the electric converter process presents several important advantages: First the complete process is carried out in a *single vessel* thereby avoiding the inconvenience, and loss of time, heat, and metal contingent on transferring molten steel from one furnace to another and also avoiding the necessity of twice heating the same metal; second, the attractive feature of the basic Bessemer process, namely the rapid elimination of phosphorus, may be taken advantage of without incurring its disadvantages in the loss of metal by oxidation and danger of over-blowing the steel; third, specially skilled operators are not essential to success of the process as there is no danger of over-blowing; fourth, high sulphur iron can be used and this alone is a most important feature because of the large amounts of ore high in sulphur; fifth, the necessity of

removing one slag and replacing it by another is avoided; sixth, the additions necessary in other processes are either greatly lessened or entirely avoided and also the losses attending those additions; and there are other advantages, among them being the ability to give the molten metal a killing treatment and to closely regulate its temperature all in one single furnace.

Little has been said in this paper about furnaces. In the tests of this process various types have been used, including the induction type to which reference has already been made. The process is at present installed for test in a 2-ton furnace. The induction furnace has shown important advantages, in that it produces the heat where most heat is needed and does so without the heavy electrode cost attendent upon arc furnace operation. In the operation of this process in large induction heated furnaces, we believe that less than 30 kw.-hours per ton of steel will be required. This may sound very radical, yet when it is remembered that steel can be kept molten in induction furnaces at the present time with an expenditure of about 80 kw. of power per ton and that it has been possible to carry out the process of this paper in less than one-third of an hour, the estimate is very reasonable. Such a low power consumption as 30 kw.-hours per ton, costing, at ½ cent per kw.-hour, only 15 cents per ton, makes the use of electric heat assume an entirely different aspect in the development of a competitor of the converter or open-hearth furnace.

The substitution of a gas containing carbon monoxide and carbon dioxide for air does not involve as great a change in present methods as at first it may appear to do. Such gas as is needed to carry out this process is available from cupolas or blast furnaces or may be made in a very simple gas producer. Blast furnace gas is preferably modified by mixture with stack gas, since the percentages of carbon monoxide in blast furnace gas is usually much higher than required. The process itself, at least in so far as the elimination of carbon is concerned, is a gas producer process, the off-coming gas being richer in CO and lower in CO_2 than when blown into the metal; and this fact opens the possibility of using the gas over and over by burning a part of it to maintain the desired composition.

On the facts presented in this paper, on the tests of the pro-

cesses which have been made and the success that has attended those tests, it seems reasonable to conclude that the application of electricity to our metallurgical processes not only will result in a tremendous saving of metal, material and labor which is now being wasted, but that it will make possible a higher quality of product at a considerably lessened cost.

DISCUSSION.

PROF. J. W. RICHARDS: I am very much interested in Mr. Greene's statement about the terms, "oxidizing," "neutral" and "reducing." It is important in metallurgy that we should keep these terms precise, by referring them to the material under treatment. For instance, in the blast furnace the atmosphere around the tuyeres is highly oxidizing for carbon and highly reducing for iron oxides. That is a condition somewhat similar to the one Mr. Greene tries to maintain; but in the blast furnace it is done by air, and in Mr. Greene's process it is done by gas. As to the removal of the phosphorus and sulphur by the addition of lime, at low temperatures, I have always regarded that reaction as not only a positive action, a pushing action, as you might say, but also as a pulling action. The removal of these impurities requires a pushing and a pulling action to get them out; with the pushing influence of the oxidation and the pulling attraction of the slag, acting together, the two will produce results which will not be accomplished by either one alone. If you have not the proper slag, the pulling factor is absent and the phosphorus or sulphur will not come out. You must therefore use slag of a suitable chemical composition, and then with the pushing of the oxidation and the pulling of the slag acting together, the two influences will do the work which neither one will do alone.

It is important, in attempting the removal of any impurities (except carbon) from iron, that you have the two factors present, a proper chemical combining influence and also the proper slag to hold the material when it is thus eliminated from the metal.

MR. A. E. GREENE: In the blast furnace, air is blown into contact with the white-hot coke and results in an atmosphere which contains probably more than 35 percent of CO and less than 1 or 2 percent of CO_2, and it can hardly be said that this atmosphere corresponds to the one used in the process I have described. This atmosphere in front of the tuyeres is not oxidizing for carbon. The air, before it combines with the carbon, is oxidizing, but it is oxidizing not only for the carbon, but also for the metal. The condition of things in the blast furnace in front of the tuyeres is better understood when it is remembered that there is sufficient coke there to take up not only all of the oxygen of the air, but also the oxygen from any iron oxide that may exist in that part of the furnace.

MR. H. D. HIBBARD: I notice that the title of the paper is "Electric Steel Processes as Competitors of the Bessemer and Open Hearth." To be a competitor means, in a business sense, that one must either give a better quality for the same money or the same quality for less money. I would like to know from which of these points of view he considers his electric process a competitor, and, if so, how much and in what way?

MR. GREENE: It is going to take time to develop a competitor of present processes, but the losses of metal that go on today are very great. To answer Mr. Hibbard's question, I think that the electric furnace will ultimately compete not only in the production of high grades of steel, but also in the production of ordinary grades such as open-hearth steel. Suppose there is 4 percent of iron lost in the conversion of pig iron into steel, the value of that 4 percent of steel would be something like 60 cents a ton, at ¾ cent a pound.

The consumption of power to carry out such a process as the one I have described, assuming we get the efficiency we have already obtained on a small scale, will be only about 30 kw.-hours per ton. We believe we will get that, and 30 kw.-hours of electricity at ½ cent per kilowatt-hour means 15 cents a ton. Of course, there are other things to be considered which I have not spoken of and which would further cut down the power cost.

PROF. RICHARDS: As far as the removal of sulphur is concerned you certainly have to get calcium out of the lime, and

you get eventually calcium sulphide. Therefore you are practically reducing lime to the state of calcium. Carbon, with its heat of oxidation, pulls in one way, while sulphur, tending to unite with the calcium, pulls the other way, and the two forces acting together determine the reaction. In the case of the phosphorus, you cannot remove it unless you have excess of lime or iron oxide in the slag to combine with it.

Mr. Greene: We are familiar with the process of putting carbon on top of an electric furnace slag to reduce the phosphorus and enable the slag to take up the sulphur at the same time. In most cases this process has resulted in reducing the phosphorus back into the metal. By using a reducing gas the phosphorus is not taken back into the metal, and the sulphur is kept out at the same time. Another interesting fact is that the slag we have examined has contained more phosphorus than any basic open-hearth slag I know of.

A paper read at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, Saturday, April 8, 1911, President Wm. H. Walker in the Chair.

A NEW TYPE OF ELECTRIC FURNACE.

By Carl Hering.

In ancient times when war and conquest were the chief occupations of man and were the chief goal in life, it was customary to make slaves of the captured enemy. While this is not a good moral principle to be recommended when our fellow men are the victims, yet it may sometimes be a good principle to adopt in dealing with inanimate things and forces. If for instance our goals in a problem are seriously interfered with by unexpected opposing forces or exasperating phenomena, it may sometimes be possible and profitable, particularly if these new forces are formidable, to make a slave of such an enemy and make it do our bidding.

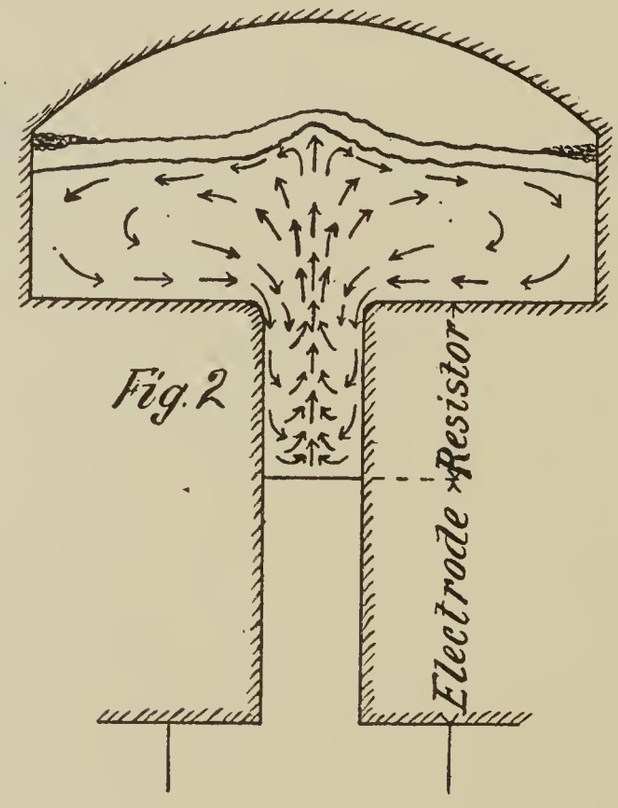
Some years ago a furnace project which was being developed by the writer, was a complete failure because a heretofore unknown or unrecognized force manifested itself unexpectedly, which acted to locally contract the cross section of the liquid resistor thru which the current was passing and in which the heat was being generated; this contraction or pinching frequently resulted in complete rupture, thereby limiting the temperature which could be generated, and on account of the appearance which it gives the conductor, the writer gave it the name "pinch phenomenon" by which it has since become generally known. This electromagnetic force acts from the circumference to the center of the conductor, and in a direction perpendicular to the axis.

As this new and unexpected force was found to be quite formidable in amount, the writer, some years ago, prompted by a desire to make this exasperating enemy his slave, devised the following method to put this force to good use.

Let the circle, Fig. 1, represent the cross section of a cylindrical conductor; these forces will then tend to act radially as shown by the arrows. If now the conductor be made to be a ver-

tical column of liquid as, for instance, the part marked "resistor" in Fig. 2 consisting of a hole in a non-conducting material closed at the bottom by the electrode and filled with the liquid, then these forces will act horizontally and perpendicularly to the axis along the whole length.

If the text books were correct in saying "like currents attract," the mutual attractions of the parallel elemental currents in such



a conductor, which produce this radial force, would simply increase the current density in the center. But as the writer has repeatedly pointed out, this attracting force acts not on the currents *per se,* but on the material constituting the conductor, and for this reason it is the liquid particles constituting this cylindrical conductor, and not merely the currents, which should be moved bodily from the circumference to the central axis; hence they should create a suction near the periphery and a pressure at the center.

Moreover, by hydraulic action these radial forces should in turn produce corresponding longitudinal forces at the center and at the periphery, and as these axial or vertical forces cannot expend themselves at the bottom, they should do so at the top, thereby producing a veritable fountain, as shown in Fig. 2, the liquid flowing up in the center and down at the periphery, about as shown by the arrows; moreover, the direction of this hydraulic flow is independent of the direction of the electric current, hence is the same for direct or alternating currents. This fountain or squirting action was therefore a prediction by theory; a subsequent test showed that the prediction and hence the theory, was correct; the forces and the consequent squirting action turned out to be even considerably stronger than was hoped for. It in fact constitutes a true valveless, electromagnetic pump.[1]

It will readily be seen that this new phenomenon, which was colloquially named the "squirt phenomenon," is admirably adapted to be made the basis of a liquid resistor furnace. If such a column is made the resistor in which the heat is generated by passing the current thru it by means of an electrode at the bottom, the heated liquid will be rapidly expelled and forced to the top against the blanket of slag, while the cooler liquid at the bottom will be sucked down into the hole near the circumference to be in turn heated and immediately expelled with considerable force. With energetic circulation thru the resistors, the fatal objections to the use of liquid resistors could be overcome.

In practice one would naturally use two holes, one for each electrode, as that reduces the depth of the hole to one-half. The proportions of the hole, that is, the ratio of the section to the length, are of course determined by the resistivity of the material, the amount of heat to be generated, and the relation of the volts to the amperes; the actual dimensions are therefore still a matter of choice. The ejecting force, or "squirting force," increases with the square of the current and diminishes as the cross section increases. It will be seen therefore that there is very fortunately some choice left as to the dimensions of these "flowing resistors," as they might appropriately be called.

In most materials there is apparently a very rapid rise of

[1] Dr. E. F. Northrup was the first to suggest and produce a vertical fountain by means of this pinch pressure, but the arrangement was typically different and could not be applied to furnaces.

resistivity with the temperature, which is very favorable to the proportions of such resistors, as is also the apparently very rapid increase of the specific heat of iron at the higher temperatures.

An analytical investigation of the relations of the various factors which determine the dimensions, reveals some interesting and unexpected results. These will be described in a subsequent paper.

The advantages of a furnace based on this principle are numerous. It is ideally simple and cheap, consisting merely of a crucible or hearth with two suitable holes in the bottom plugged with the electrodes. The heat is generated in the material itself, which is just where it is wanted; moreover it is generated in the most rational place, namely at the bottom and not on the top surface; it is conveyed and distributed mechanically, so to speak, thruout the melted mass, and this conveyance of heat is immensely more rapid than it would be by mere conduction or by the slow flow due to differences of density; hence a charge is treated and finished rapidly, whereby the output of the furnace per day is increased and the losses of heat per ton are proportionately reduced. As far as is known now, there is no temperature limit except that of the failure of the refractory lining, as the pinch effect can no longer limit the temperature.

This very active agitation and circulation of the liquid mixes the product rapidly with any of the refining ingredients which may be added, and tends to make the product very homogeneous. Every particle of the liquid is in turn, and repeatedly, brought to the surface where mechanically suspended impurities and gas bubbles are expelled and forced into the slag, and where the metal is exposed to the chemical action of the slag, which is so desirable and important in the refining of steel; the fresh and highly heated surfaces thus exposed to slag action are of course enormously greater than in a still bath. The top surface of the metal may of course be made as large as one desires. The temperature at the surface of contact of metal and slag, on which temperature the slag action depends, is certainly maintained better when the heat flows up naturally from the hot metal to the cooler slag, than when it is forced to flow down unnaturally, from the hotter slag to the cooler metal; aside from the fact that heat in liquids generally prefers to rise than to be carried down, there would in

the latter case necessarily be formed a layer of cooler slag in direct contact with the metal, and even if quite thin this would undoubtedly act as a blanket of high thermal resistance, necessitating heating the slag to very high temperatures in order to force the heat thru this resisting layer with the desired rapidity.

Other advantages besides these lie in the fact that the electrodes are very cheap, are not consumed, and as they may be made of metal they are far more economical in energy loss than carbon or graphite would be. No moving and adjusting of the electrodes are required. The interior of the furnace may be made as small as the quantity of material to be held requires, hence the thermal efficiency of the walls of such a furnace could no doubt if desired be made to reach the practical maximum of all types of furnaces. Moreover, as the heat is rapidly distributed mechanically thruout the mass, the maximum temperature need be no higher than that required for the desired metallurgical or chemical action, hence the heat losses, which increase so rapidly with the temperature, are correspondingly reduced; in this there is a great advantage over arc furnaces, in which the temperature is necessarily that of the vapor of carbon, hence immensely higher than what is needed.

The regulation is simple, rapid, and in fact ideal; the resistance does not change appreciably with varying amounts of metal in the hearth; the resistance of the resistor, as determined by the voltage and amperage, may perhaps in some cases be an indication of the progress of the metallurgical treatment; and owing to the very rapid circulation one can feel sure that the treatment is uniform thruout the whole mass.

There is an interesting feature in the fact that when the electrode is made of the same diameter and material as the resistor, the furnace should tend to become self regulating as to temperature. When, for instance, the temperature becomes higher, the electrode automatically becomes longer and the resistor therefore shorter, whereby less heat will be generated; and the reverse when the temperature becomes lower. The place where the electrode ends and the resistor begins is, of course, that section across which no heat flows; the heat generated below this section flows out to the terminal and that generated above it flows into the furnace; it is this plane that automatically moves up or down.

The hottest liquid is that in the center of the resistors and is therefore not in direct contact with the refractory lining.

The friction of liquid against liquid, in the interior of the conductor, is far less than might be supposed, provided the liquid is in a very fluid state. The rapid flow is not along the walls of the hole, but in the center where it, of course, causes no wear. Whatever friction there is, converts the mechanical energy into heat, and is therefore not lost.

The counter e. m. f. which must necessarily be generated by the movement produced, is an advantage as it shortens the resistor, and the energy corresponding to this counter e. m. f. of course also ultimately generates heat by friction, and is therefore recovered. Some of the electrical energy is therefore converted first into motion and then into heat; the greater this part the better.

By using a bath of some suitable metal in the bottom of the furnace as the prime receiver of the heat, the furnace is adapted to be used to melt non-conductors like glass, or to heat granular ores, reduce and volatilize such metals as zinc and arsenic from their ores, etc. By dissolving carbon in the iron in one part of a bath and the oxide in another part, iron can be reduced from its ores, and the CO gas produced can be burned to preheat the ore, whereby the total energy of the carbon may be utilized, notwithstanding the fact that an authority recently said this was theoretically impossible.

The power factor can of course be made very high, probably practically unity, and unlike in the induction furnace the frequency need not be abnormally low.

The squirting action operated very satisfactorily the very first time it was tried in a furnace. Even a moderate pinch pressure was found to produce a very active circulation, probably more than ample for most purposes. The top surface of the metal shows two little agitated hills with two or four low points between them constituting whirlpools in which the floating dirt all collects. The action resembles the rapid boiling of water when the heat is concentrated at two spots, except that there are no gases formed and it is therefore quite noiseless.

When badly proportioned the columns are apt to pinch off, causing rapid "makes and breaks;" this so greatly reduces the amount of heat which can be generated, that there is danger of

freezing. Such repeated breaking of the circuit should by all means be avoided. Several times a charge was left to freeze in the furnace over night and yet was readily started the next day from the cold state, thus showing that the resistors do not part in shrinking.

An interesting feature of the principle on which this type of furnace is based is that, contrary to the more usual cases, the larger the furnace the better, and the less will be the difficulties, because the resistors then become shorter and thicker. The principle does not lend itself so well in this form to small furnaces, as the resistors then tend to become long and thin; there are however modifications to be used in such cases, which need not be considered now. This new principle naturally opens up a new field and there are, of course, many modifications which at once suggest themselves, which will be tried in due course. It would be quite simple, for instance, to add gaseous fuel heat, or the heat of an arc, in the upper part; or to add the electrical parts to existing open hearth or other furnaces, or to pots or ladles for transportation, and use the electric heat only for the final treatment.

The transformer is best attached directly to the bottom or side of the furnace, as the furnace currents are of course of low voltage, hence large in amperes. The flexible connections to a tilting furnace then consist merely of the two thin primary wires. The furnace is readily adapted to three phase currents; the only change is that there will be three holes and electrodes instead of two. This is an advantage because, for the same current in each electrode it shortens the resistors by one third. A two phase current may be readily transformed into one of three phases by means of a Scott transformer.

Under all conditions there should always be reached a stable state of temperature in the resistors, at which the heat generated in them is equal to that carried out of them mechanically; the best conditions must be determined by practice; fortunately there is a considerable range of latitude in the dimensions which could be chosen.

The following is a list of some of the objectionable, troublesome or undesirable features of arc, induction, and simple resistance furnaces with liquid resistors, and it will be seen that they would all be avoided entirely or at least lessened, in the present type of furnace.

Among the disadvantages of arc furnaces may be mentioned the following: the handling, feeding and adjusting of the electrodes; their cost, because they are consumed; the breaking off of their ends in the furnace; the handling of the hot stubs; the difficulty and expense of making good connections with the terminals outside of the furnace, thru which terminals the electrode must be capable of being moved; the water cooling of these movable terminals above the furnace; hence the possible danger of water running into the furnace; the wasting away of the electrodes on their sides; the contamination of the product by the material of the electrode which cannot be of metal; the carbonaceous atmosphere; the unnecessarily high temperatures, and the consequent additional losses thru the electrodes and the roof of the furnace; the unnecessarily large inside volume of the furnace, which increases the losses; the heat is applied at the top, hence travels down chiefly by very slow conduction, aided somewhat by a local agitation immediately under the arc; there is therefore no gravity circulation, hence the distribution of the heat is necessarily very slow and uneven; the heat must pass thru the slag which is a bad conductor, to the metal which is a good conductor, instead of the reverse, which would be more rational; hence the heat convection to the metal is necessarily slow; this means greater loss of heat per pound of product, and a larger furnace; complications arising when three phase currents are used; the difficulty in regulating the current of an arc, and the cost of apparatus for doing so; the troubles when the arc goes out; the attention required to prevent this; an arc furnace cannot well be used for zinc, arsenic, glass, etc.

Among the disadvantages of induction furnaces may be mentioned the following: the cost; the bad power factor, and necessarily poor transformer; the necessarily poor heat insulation; it must be dismantled to start cold; the necessity of retaining a large part of the charge for starting the next run, or it must be started with a relatively large part of the charge heated elsewhere; the limitation of temperature by the construction and by the pinch phenomenon; the maximum temperature may therefore not be high enough for some purposes, as for instance, for the melting of aluminum, which, owing to its lightness, pinches off when current only slightly above that required for melting is used; all

of the charge conducts the current, hence the charges must be small or the possible variations of the current very great; unequal heating when not perfectly level; no very active longitudinal circulation, hence the chemical actions are slow, involving a smaller output per day and therefore a greater heat loss per pound; no large open space for slag action, except by introducing complications; these require additional current to be introduced by means of electrodes, and the difficulties then arise of getting rapid circulation, as well as some of the other troubles of electrode resistance furnaces which it was the very purpose of the electrodeless induction furnace to eliminate; expensive complications when three-phase currents are used; apparently not applicable or practicable for ferro-alloys, zinc, glass, ore reduction, etc.; the difficulty of good insulation of the high tension current.

Among the disadvantages of resistance furnaces having electrodes and containing fused material, may be mentioned the following: serious limit of temperature and speed of heating due to pinch phenomenon; contamination of the product by the material of the electrode if carbon or graphite; great changes of current required with increasing quantities of reduced materials; hence small charges or very great regulation; small slag surface in narrow channels, or if channels connect with a large hearth, then the difficulty of getting rapid circulation from the heating channel to the hearth; the cost of apparatus for doing the same; complications arising with three-phase currents.

DISCUSSION.

Mr. G. H. Clamer: I do not think Mr. Hering made quite clear to you the difference between the resistor and electrode in the furnace which he described. The electrode is made of metal, and preferably of the same metal which is to be melted in the furnace. It is so proportioned that the heating effect of the current passing through it shall raise the end of the electrode to a temperature which is as nearly as possible equal to the temperature of the molten metal in the resistors, so that the heat loss through the electrodes shall be reduced to a minimum.

The two resistor tubes are so proportioned in diameter and length that the heavy current passing through the columns of metal in the tubes rapidly brings these columns of metal to the liquid condition, and produces therein the "pinch" effect, whereby the metal is squirted out of the tubes at the centre of the column, as he describes, it being further necessary that the current be so proportioned in respect to the hydraulic head of the metal above the tubes that no breaking of the circuit occurs, as this would entirely defeat the extremely useful effect of the "pinch," which in this type of furnace results in complete circulation of the bath.

I have had the good fortune to witness the phenomenon described by Mr. Hering, and can say to you that this force is no mere theoretical force, but is in reality a vigorous agitation and circulation. I have seen a furnace made in accordance with Mr. Hering's invention started by casting in liquid metal in sufficient amount to fill the resistor tubes and bottom of furnace to a depth of about two inches. In this way electrical connection was established with the electrodes and a circuit formed by the columns of metal in the resistor tubes and the body of metal connecting them. The metal after being cast in was allowed to become perfectly frozen and black. The current was then turned on, using five volts and approximately 3,000 amperes, the resistor tubes being ¾ in. (2 cm.) diameter and 4 in. (10 cm.) long. In a very short time the metal was brought to a dull-red heat and the current was gradually raised until there were somewhat over 5,000 amperes passing through the circuit, the temperature of the metal in the meantime becoming higher and higher until it finally melted in the resistor tubes and the squirting action commenced. As soon as the squirting action began the remaining metal in the bottom of the furnace was soon melted and the furnace was ready for continuous operation.

The tubes in the particular furnace described were made of alundum, a material which it has been found admirably resists the high temperature in the resistor tubes and also the eroding action of the metal circulating in them. The tubes have also been made of magnesite, which gave very satisfactory results.

It would be reasonable to suppose that these tubes would become rapidly destroyed, owing to the circulation of the metal in

them, but very fortunately the "pinch" action is of such a nature that the metal is forced with violence from the centre of the column and a vacuum is produced at its periphery, so that the inflowing speed of the metal is slow, and the action upon the tubes, therefore, very slight.

This type of furnace seems to be applicable for a great many operations, and eliminates many of the undesirable features of other types of furnaces, while the fact that the heat is generated in the metal itself, that the heat is applied at the bottom of the furnace, and that perfect circulation of the bath takes place, would seem to give it decided advantages over existing types.

MR. BECKMAN: How does the lining stand up?

MR. HERING: We have used alundum tubes and they worked well, although they are liable to crack. We also used magnesite powder, packed while in a plastic form; after being heated, it formed an extremely hard, smooth, glossy layer on the inside of the tube and was very satisfactory.

MR. L. E. SAUNDERS: I want to call attention to this circulation of the metal, and ask Mr. Hering if the circulation is just as rapid in the larger size as it is in the smaller-sized furnace. I believe that in the induction furnace, especially in the Colby-Kjellin furnace, as the size goes up the rotating movement of the metal decreases, that is, it is not so rapid in the larger sizes as it is in the smaller sizes, and this is an important matter in that type of furnace, because of the wear on the refractory lining. The rapid circulation digs into the lining, no matter how refractory it is. It is solely an abrasive action and not a heat action.

MR. HERING: The phenomenon is much better adapted to a large furnace than to a small one. Some of the difficulties which have been encountered were due to the fact that we were working with too small a furnace. As the furnace gets larger, the proportions become more favorable, because you can have enormous pinching pressures without fear of pinching off the column.

PROF. J. W. RICHARDS: I am pleased to see the application of this new force in Mr. Hering's furnace. I would call attention to the fact that in the Girod furnace we have a bath of metal heated principally by an arc above, with an electrode through the

hearth, intentionally made small enough to be partly liquid and partly solid; so that the electrode in action is partly liquid, and there is a dividing line below which it becomes solid.

In the part of it which is liquid, I think perhaps that, possibly without knowing it, Mr. Girod may have had some of that same squirting action. That would not detract at all from the merit of Mr. Hering's discovery of basing the working of a furnace on that heating and stirring principle alone.

In our Transactions there have been published the drawings of the Gin self-circulating induction furnace,[1] which show a current passing through inclined small passages, and Mr. Gin describes in that paper the amount of circulation which is caused by the use of these inclined passages. He attributes it to the greater heating of the metal in these passages, causing the metal in them to rise and thus to circulate. That is what he says in his paper; he says it is a self-circulating furnace, in which there is a circulating current caused by the superior heating of these small passages.

Without knowing it, if Mr. Hering's explanation is correct he may have been utilizing this force, because in these passages he has the same pinch force working which creates the circulation in Mr. Hering's furnace. He has told us how fast the metal circulated in these tubes, and ascribed it to the overheating or the extra temperature therein.

Mr. Hering: I am sure there could not have been any pinch pressure circulation, judging from the proportions in the pictures of Mr. Gin's furnace; if he had a large enough current to produce any squirting, the resistors would have gotten too hot and the metal would have volatilized; the passages are altogether too long. Moreover, in his arc furnace the two arcs are in series with the tubes, hence the current must be the same; the arc current is too small to produce any pinching effect. If Prof. Richards were familiar with the quantitative relations involved, he would not have made these statements. Proper proportions are essential to get the desired results. I am sure Mr. Gin could not have had through these tubes anything but the gravity circulation which he describes.

[1] These Transactions, **15**, 205 (1909); **12**, 442 (1907).

Mr. H. K. Hitchcock: I am quite struck with the fact that in the remarks of Mr. Hering and Prof. Richards in regard to the circulation in the Gin furnace, which are quite correct in regard to the electrical end, they have failed to take into consideration the hydraulics involved.

In Mr. Hering's furnace he has a solid end which prevents any flow of the liquid in the downward direction, whereas in the Gin furnace, if there were such a phenomenon as the pinch phenomenon, there is no reason why the increased pressure should not force the liquid back into the deeper column. Instead of this pinch force pressure, it is the difference in temperature in the columns which causes the circulation.

I do not know that I make this clear, but in order to get the circulation due to the pinch phenomenon which Mr. Hering describes, it would be necessary to have a bottom in the canal so that the metal could not go in that direction, but must go in the other. In the Gin furnace there would be no reason why it could not go back into the deeper column, except the difference in weight due to the difference in temperature. This difference in weight would tend to cause a circulation.

Mr. Hering: I tried just that very arrangement, and it does not work, as Prof. Richards claims so positively that it does.

Mr. B. G. Worth: Is it not sufficient to say that the two forces balance, that the pinching effect works both ways, up and down? I wish to ask Dr. Hering if he has deduced a law which connects the current density and the pressure in this phenomenon; that is to say, do you know the pressure which produces the squirting, and how does it depend on the density of the current in the conductor?

Mr. Hering: Dr. Northrup has developed the mathematics of the pinching force; the quantitative formula is known very definitely. In all my experiments I knew exactly what the pinch pressure was. The pressure at the center varies as the square of the current and inversely as the section. I published these formulas recently.[2]

Mr. Henry Hess: In connection with some investigations that I asked Dr. Hering to make for me on the pulverization of

[2] Met. and Chem. Engineering, Feb. 1910, p. 86.

certain metals of low melting points I also looked into the general literature on the subject, and procured, through a German source, the "Technische Auskunft," a lot of material. In that was included a copy of "L'Industrie Électrique," No. 224, of April 25, 1901, and an article, on p. 178, "La Pulvérisation Électrique des Métaux." This gave a description of a method employed by Paul Bary for pulverizing the metal by passing through a narrow stream of the liquid metal an electric current of sufficient strength to disrupt the stream—pinch it off—fine metallic powder being thrown off at the instant of rupture.

In that article certain mathematics of the disrupting force are also given.

Mr. P. Kemery: If you adapt your furnace for practical use, how would you keep the bottom portion in repair?

Mr. Hering: Just as in any other furnace. All that I attempt to give in this paper is a general description of the phenomenon and not the details of any particular furnace. The tapping would be done by tilting, as usual. It can be made a tilting furnace by attaching the transformer to the whole tilting portion; or it can be tapped with a regular tapping-hole just above the resistors; the liquid should be left in the resistors.

Mr. Kemery: How would you keep it in repair?

Mr. Hering: One would repair the worn-out parts the same as in any other furnace in which parts wear out.

Mr. A. L. J. Queneau: I doubt very much if in the Girod furnace there would be a very large circulation induced at the electrodes, because of the small amperage per square inch. In the Girod furnace, if I understand correctly, you have between 40 and 50 volts, therefore the amperage is rather low, while in the pinch furnace you deal with a small voltage and enormous amperage.

Mr. A. H. Strong (*Communicated*): One of the advantages of this type of furnace certainly is that the temperature at the point of contact of metal and slag, on which the rate of refining depends, is better maintained when the heat flows out in a natural way from a hot metal to a cool slag than *vice versa*. Further, as the heat is rapidly distributed mechanically through-

out the mass, the maximum temperature need be no higher than that required for the desired refining operation.

In an induction furnace the power factor can be 0.7 or 0.8 when using 25-cycle current by combining the induction furnace with the resistance type or aiding the low power factor with rotary condensers. This high power factor makes a very normal and inexpensive transformer.

MR. HERING (*Communicated*): Replying to Mr. Saunders' question, the strength of the force which causes the circulation is entirely under the control of the designer. It can be made larger or smaller in the larger sizes, as one desires. It is a mere matter of proportions.

As to the wear on the walls, the rapid flow is in the center of the column, where there is, of course, no wear; the flow down along the sides is very much slower. It is intended, however, to so design the furnace that these holes may be easily repaired.

Prof. Richards remarked that there may have been some of this squirting action in the Girod furnaces. Prof. Richards is evidently not familiar with the laws concerning this pinching force. In the Girod furnace the current is that for the arc, and this is far too small to produce any appreciable pinching force at the upper end of the lower electrode. It requires high current densities to produce this squirting phenomenon; the fact that the hot end of the iron electrode is melted in the Girod furnace is no reason why there may have been a pinch effect in that portion.

Prof. Richards is also mistaken in his efforts to show that Mr. Gin had anticipated the use of the pinch pressure to produce circulation, because a current great enough to produce a perceptible squirting action in such very long, slender tubes would no doubt volatilize the metal, as it would heat the metal faster than the heated metal could flow away. Moreover, the inclining of the tubes shows that Mr. Gin relied on gravity circulation, and he even says so. Hence, Prof. Richards is mistaken when he says so positively that Mr. Gin "has the same pinch force working which creates the circulation in Mr. Hering's furnace." Moreover, the squirt in such a tube would be outward at both ends, as Mr. Worth has stated; hence there would be a stagnant

place somewhere within it where the metal would not be circulating and hence would immediately overheat and vaporize.

Mr. Gin himself, moreover, actually says that the circulation in his channels is due merely to differences in densities. In these Transactions, Vol. 12, 1907, p. 443, near the top (a reference not specifically cited by Prof. Richards), Mr. Gin uses the following words, as translated by Prof. Richards himself, namely, that the Joulean heat, being greater in the restricted inclined channels, produces "a difference of density in the channels resulting in an ascensional movement and continuous circulation in one direction thruout the series of canals." Moreover, to use the pinch effect there would be no need in inclining the tubes.

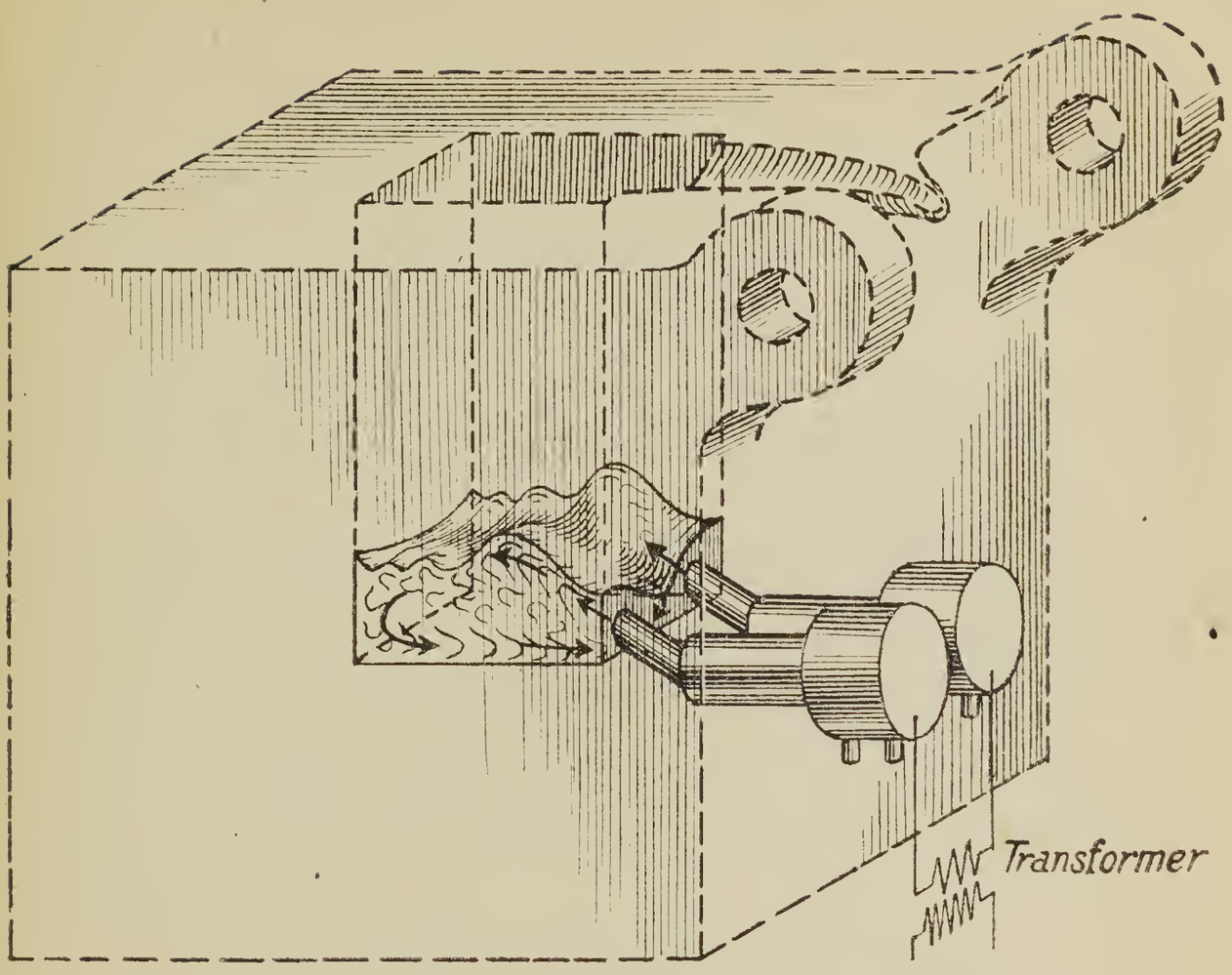
But Mr. Gin later even actually disclaims using the pinch effect. In these Transactions, Vol. 15, 1909, p. 206, near the top, again as translated by Prof. Richards himself, Mr. Gin says, in referring to these heating channels, that "a very high temperature can be obtained *without fear (sic) of the 'pinch' phenomenon* in the heating passages." [Italics mine.—C. H.] Again he adds a few lines below that the velocity in these heating channels varies with their inclination, which of course implies that the circulating force is gravity and not electromagnetic.

But whether or not the pinch pressure acts in his furnace, Mr. Gin certainly did not describe or disclose its application.

Prof. Richards should, in my opinion, have considered the matter more carefully before making such unfounded claims of priority in print.

Replying to Mr. Strong's remarks, it is true that the heat is developed in only a part of the charge, but the circulation is so very energetic that the heat is rapidly distributed thruout the whole mass. Some designers of induction furnaces differ very decidedly with Mr. Strong as to the sufficiency of the lengthwise circulation in the channels of an induction furnace. The prevailing opinion seems to be that this circulation is quite slow and decidedly less than is desired.

In reply to a member who, after the meeting, claimed that I was mistaken in attributing the circulation to the pinch effect, and who alleged that it was only simple gravity circulation due to differences of density of the differently heated parts, as in heat-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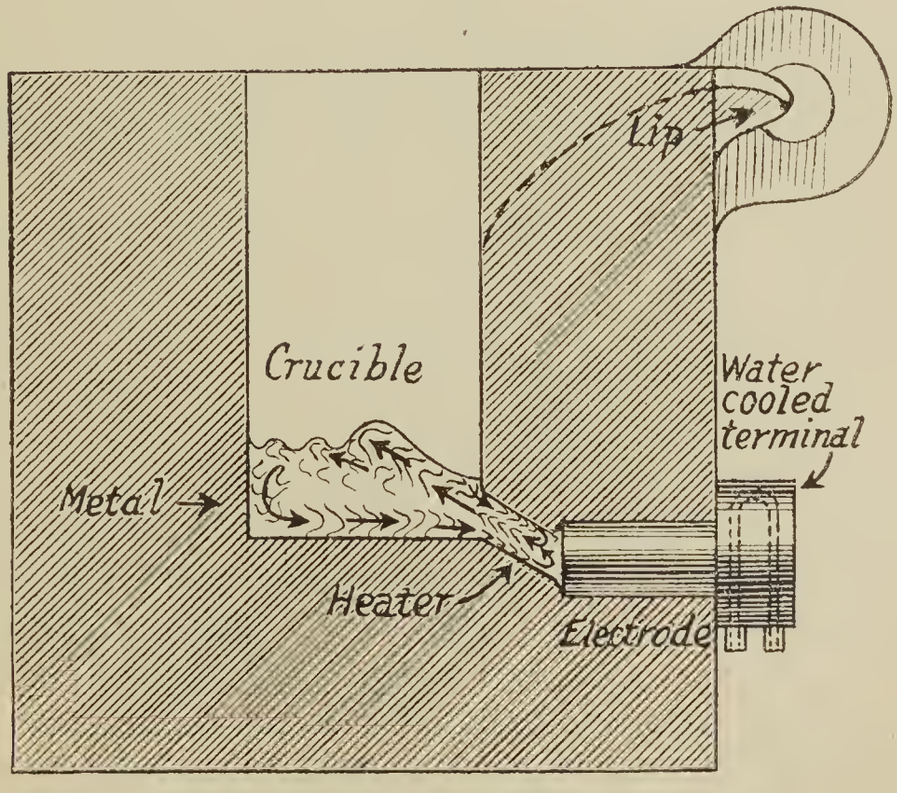
Lip
Crucible
Water cooled terminal
Metal
Heater
Electrode

ing water, I need only say that if he had seen the almost violent agitation, with the metal surface sometimes at 45°, flowing like water thru rapids, he would, I am sure, unhesitatingly withdraw his claim. The suction is so strong that in one case air was sucked in at the bottom of the resistor, thru a leaky tap-hole, with a whistling noise; at another time, when the layer of liquid metal was not deep enough, small pieces of charcoal were sucked down into the resistors; gravity cannot produce a suction. To rely on gravity circulation would make the furnace so large and so slow-acting that it would be entirely out of the question to use it commercially.

In reply to numerous inquiries made to the writer concerning the general construction of furnaces based on this principle, the accompanying outline sketches are added here. The ghost sketch shows the highly agitated molten metal in the bottom of a crude form of crucible, and also the arrangement of the two resistors in which the metal is heated and is rapidly expelled by these electromagnetic forces; also the metallic electrodes with their water cooled terminals. The second sketch shows the same in vertical cross section thru one of the two electrodes, and indicates the character of the circulation. The transformer is shown only diagrammatically; in a tilting furnace it would preferably be attached to furnace. The furnace is shown as one tilting around the nose as a center, so as to cast directly into molds.

A paper read at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 6, 1911, President Wm. H. Walker in the Chair.

A NEW ELECTRIC RESISTANCE FURNACE.

By Francis A. J. FitzGerald.

The furnace which forms the subject of the following note was designed originally by Mr. John Thomson and the author for carrying out the Imbert zinc melting process; but the experiments made with it showed that it would also be applicable to other kinds of work. It is not intended to discuss the problem of zinc smelting, but in order to make clear the conditions governing the design of the original furnace, a brief outline of the Imbert process will be given.

It is well known that if zinc sulphide and metallic iron are heated together to a sufficiently high temperature, the following reaction occurs:

$$ZnS + Fe = Zn + FeS$$

It appears, however, that this reaction is incomplete unless there is a large excess of iron present, or unless the temperature of the reaction is very high. Imbert discovered[1] that, by using suitable "dissolvents," this objection to the process is overcome. For example, he found that ferric oxide and iron sulphide mixed together in the proportion of one part and three parts, respectively, formed a very fluid bath at a temperature between 1000° and 1100° C., and that this bath would "dissolve" six parts of blende. Now, when the zinc blende is "dissolved" in a bath in this way and treated with iron, the reaction given above is complete and works very easily, the zinc being given off as vapor and a residue obtained which consists of two parts—a slag, formed of the gangue of the ore, and iron sulphide, which may be used for the regeneration of iron, etc.

The experiments made by Imbert were satisfactory, but the process is obviously not suitable for the ordinary zinc retort, and it was thought that an electric furnace might be used with

[1] U. S. Patent 85,579; Dec. 31, 1907.

economy. Experiments with various electric furnaces were tried, and finally the kind which forms the subject of this paper was devised.

The conditions to be met by the furnace are as follows: It is desired to obtain a bath of molten iron to which can be added a mixture of the zinc ore and the "dissolvent." The furnace must be gas-tight and must be constructed with sufficient ruggedness to withstand high temperatures and rough usage over prolonged periods. It must also be so designed that the temperature can be readily controlled, and finally the heat losses must be reduced to a minimum.

The first furnace constructed had an oblong reaction chamber which was roofed over by the resistor. This was built of carbon rods, laid transversely across the top of the reaction chamber, the ends of the bottom row of rods resting on ledges built of magnesite brick. The resistor was in contact with the furnace terminals, which were situated at either end. A charging door was provided under one terminal, while the tap-hole was under the other. The melting chamber of this furnace had a capacity of 250 kilograms (550 pounds) of iron.

Several experiments were made, but the most important was one lasting three days and five hours. During this experiment a quantity of pig iron was melted in the furnace, and it was found that, with a temperature in the bath of 1300° C., the radiation loss was about 18 kilowatts. Since the full working capacity of the furnace was 40 kilowatts, the efficiency at 1300° C. was 55 per cent., which is not bad, considering the small size of the furnace. This experiment was ended by keeping the current at 40 kilowatts without charging anything, the object being to find out how the furnace would finally fail under the increasing temperature. As was expected, failure occurred through the fusion of the magnesite bricks which supported the rods of the resistor.

After the furnace cooled, it was taken down and examined, with the result that an interesting observation was made which gave a good notion of the temperature finally obtained in the bath. The reaction chamber was lined with Dixon's graphite-clay mixture, used in making crucibles, and it was found that this had been largely converted into amorphous silicon carbide.

Various critics of a furnace built according to this plan have pointed out that an unsatisfactory feature is the risk of fusing the cover. Presumably the heat radiated from the top of the resistor, which, of course, is just underneath the roof, would be so great as to be very severe on that part of the furnace. This objection, however, is not serious, for the current density at the lower part of the resistor is greater than at the top. The carbon rods forming the lower part of the resistor are in much closer contact than those in the upper part on account of the weight of the upper carbon rods; consequently the resistance of the lower layers of carbon rods is less than that of the upper layers, and the heating effect in them correspondingly greater. The fact that the magnesite bricks below the resistor were fused at the end of the experiment, while the roof, which was built of a good grade of ordinary fire-brick, was unharmed, shows clearly the difference in temperature between the upper and lower parts of the resistor. Moreover, by means of pyrometers, actual determinations were made simultaneously of the temperatures in the bath and in the space between the top of the resistor and the roof. These showed that when the bath had a temperature of 1500° C., the temperature in the space above the resistor was only 1250° C.

In view of the fact that the final failure of the furnace was due to the excessively high temperature reached at the end of the experiment, it was concluded that for the lower temperatures required in working the zinc process, no difficulty of this kind would be encountered. Accordingly a furnace having an estimated capacity of 150 kilowatts was designed. In order to obtain a sufficiently high resistance in the resistor, it would have been necessary to give this furnace a length considerably greater than its width, which would be objectionable on account of the relatively large radiating surface that would result. Consequently the furnace was constructed with both terminals at one end and the resistor in two sections, connected with each other at the end of the furnace opposite the terminals by a graphite connector. One side of each section of the resistor was then supported on a ledge running along the side of the furnace, while the other sides were supported on a series of arches spanning the center of the reaction chamber in a longitudinal sense. By this arrange-

ment a nearly cubical form was given to the furnace, and consequently the radiating surface reduced to a minimum. The inside dimensions of the reaction chamber were approximately 1400 mm. (55 inches) square and 250 mm. (10 inches) deep. The resistor was built of rods 19 mm. (¾ inch) in diameter and 500 mm. (20 inches) long. There were seven layers of these carbon rods in the resistor, each section of which was approximately 1140 mm. (45 inches) long. The furnace was supplied with charging doors, peep-holes, tap-holes, etc., but the details will not be entered into here.

The experimental work on the zinc process was carried out at the plant of the Hohenlohe Werke A. G., Hohenlohehütte, Upper Silesia, where the electrical apparatus was installed and the furnace constructed under the author's supervision. The electric current was supplied to the plant at 6,000 volts, and was transformed by a special transformer. The construction of the plant and the carrying out of a long series of experiments occupied over three months, and the results obtained with the furnace were satisfactory. The highest temperature actually measured in the furnace was 1460° C., but higher temperatures were certainly obtained.

Very interesting experiments were made on the heat losses of the furnace. During one part of the experiments the furnace was held at a constant temperature of 1250° C. to 1260° C. for over three days. During this time the furnace contained a bath of pig iron and was otherwise idle, so that the energy generated was used simply for supplying the heat lost by conduction and radiation. The rate of generation of energy, when an absolutely constant temperature both in the bath and walls of the furnace was reached, was 33 kilowatts. If, therefore, the furnace is working at 150 kilowatts and a temperature of 1250°, the heat losses would be 22 per cent. Another experiment was made which lasted 12 hours, and during this time the temperature of the bath was maintained at about 1450° C. Unfortunately the temperature of the furnace as a whole was not constant at this time, for the temperature of the walls increased 100° during the experiment. The rate of generation of energy during this period was 42 kilowatts, which, working at 150 kilowatts, would give a loss of 28 per cent. It must be noted that the heat insulation

of this furnace was not by any means as perfect as it could be made. The thickness of the walls in the upper part of the reaction chamber was only 340 mm. (13½ inches). That a much more efficient use of the heat generated could be made by more careful attention to heat insulation was demonstrated by later experiments.

The chief weakness shown by the furnace was in the magnesite bricks which formed the supports for the ends of the resistor carbons. The temperature of the resistor is very high, as was shown by making determinations of the density of the carbons forming the resistor after they had been in use. This shows that temperatures at least as high as 1900° C. were reached in the resistor itself. In the experiments made with the Imbert process, it was shown that the most satisfactory temperature for carrying on the reaction was between 1350° C. and 1400° C. in the bath, which would not require these excessive temperatures in the resistor. Nevertheless, it was seen that the work had to be carried on too close to the limitations of the refractories, and this led to the development of a furnace of a different model, which will be more particularly described. Before considering this, however, it will be well to note some other experiments made with the rod-resistor furnace.

It will be observed that in working the Imbert process the furnace is filled simply with vapor of metallic zinc; consequently there is no danger of burning the resistor carbons. The charging devices are so arranged that air is not introduced into the furnace, so that the zinc vapor does not burn to zinc oxide, which would, of course, attack the carbon of the resistor. If, however, the furnace is used for other purposes, it might be necessary to protect the resistor from combustion. For example, if a furnace is desired for copper melting, it would be inconvenient and complicated to make arrangements absolutely to exclude air. It is better to enclose the resistor in a chamber, the bottom of which forms the roof of the melting chamber, and then make this resistor compartment air-tight.

A great many experiments were made to determine the best material for forming this combined floor and roof, which requires, above all, two qualities—refractoriness and high heat conductivity. The result was the choice of recrystallized silicon carbide tiles.

These are found to be satisfactory and to last well, even under severe usage. It would obviously be difficult to construct the resistor chamber so that it would be perfectly air-tight; so to prevent all possibility of oxidation, it is desirable to introduce an inert or reducing gas into the resistor chamber and to maintain this atmosphere slightly above external pressure. A simple method, employed with success in experimental furnaces, is to put a long pipe in the cover of the furnace and mount on this a large oil-cup with a sight feed. The oil-cup is filled with kerosene, which is allowed to drop slowly into the resistor chamber, so as to keep the latter continually full of oil gas. In one furnace constructed in this way, after two months' continuous running, the current was cut off, the furnace allowed to

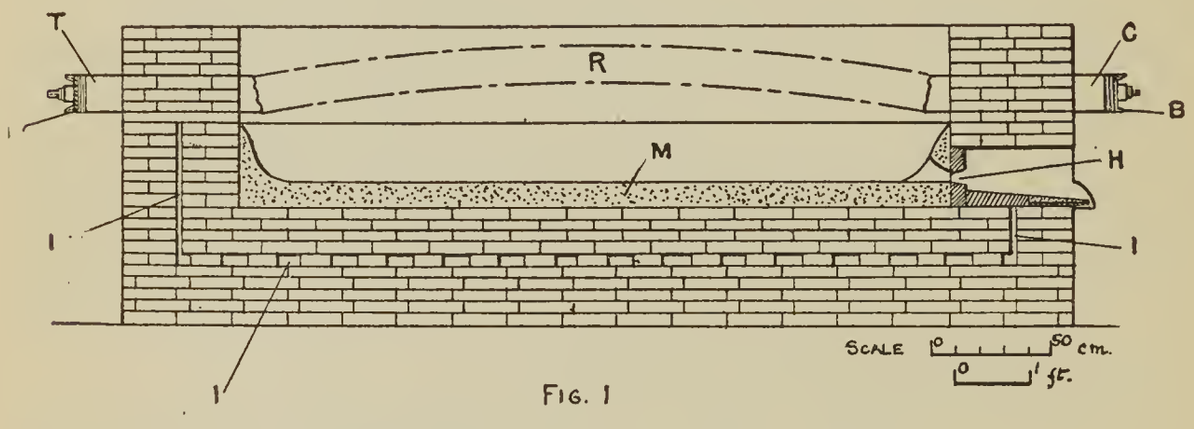

FIG. 1

cool down and the resistor chamber opened. The resistor was found to be in excellent condition, though a few repairs to the terminals were necessary. The resistor chamber was then closed, and, at the time of writing, the furnace is still running in a satisfactory manner, so that altogether the furnace has been working, with slight repairs, more than four months. This particular furnace has been used for a great number of experiments at temperatures varying from 1000° to 1500° C. (1830° to 2730° F.).

In a furnace constructed with the separate resistor chamber, several experiments were made on melting aluminum, copper, monel metal and iron, but the value of these was qualitative rather than quantitative. The furnace walls were only 230 mm. (9 inches) thick, consequently the heat losses were so great that the furnace was not by any means efficient. The object of the experiments was to study the weak parts of the furnace. They

confirmed what had been already observed, *viz.*, the weak part of the furnace was the support of the resistor.

The new model of the furnace is illustrated in Figs. 1 to 5. Fig. 1 is a longitudinal section of the furnace, the cover not being shown. Fig. 2 is a transverse section, and Fig. 3 a plan with the cover removed. The walls and bottom of the furnace are cellular as well as the cover, so that it is almost completely surrounded with an air jacket, as shown at *I* in the illustrations. *T,T, C,C* are carbon plugs which pass through stuffing-boxes in the end walls of the furnace. *T,T* are the terminals of the furnace, and are connected to the cables indicated by *P* and *Q*.

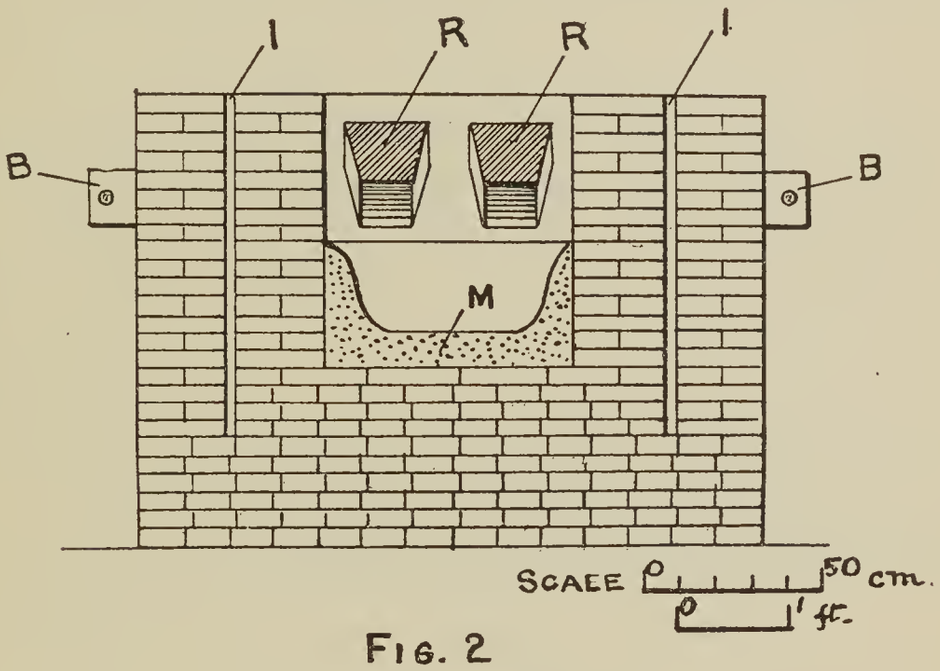

FIG. 2

C,C are simply connector electrodes which form the other terminals of the sections of the resistor *R,R,* and are connected by *E*. Bearing on the terminals *T,T* and the connector electrodes *C,C* are the channels *B,B,* which are connected to each other by the tension rods *S,S* and are insulated from the carbons. The lining of the furnace is shown at *M* and the tap-hole at *H*. The resistor *R,R* is constructed of corrugated plates (Fig. 4), where the section is shown on the left and the form in which the plates are cut on the right. Fig. 5 is a photograph of the plates set up to form the resistor. Referring to Fig. 4, it should be noted that the thickness of the corrugated plates is not the same at the top as at the bottom, but increases from the bottom up, so that when

put in place, they from an arch, as shown in Fig. 5. This arch form is not necessary, since the interlocking of the corrugated plates holds up the resistor perfectly well without any arch, but it seems to be desirable in the preliminary assemblage and also permits us to obtain a greater current density on the lower surface of the resistor.

By constructing the resistor in this manner, all contact with refractories is avoided; the support being furnished by the carbon terminals. The form of the plates is not, however, solely designed to provide an interlocking device, but also to give a high contact resistance. In one of these furnaces which was built for zinc smelting at Hohenlohehütte, Upper Silesia, there were 71 of these

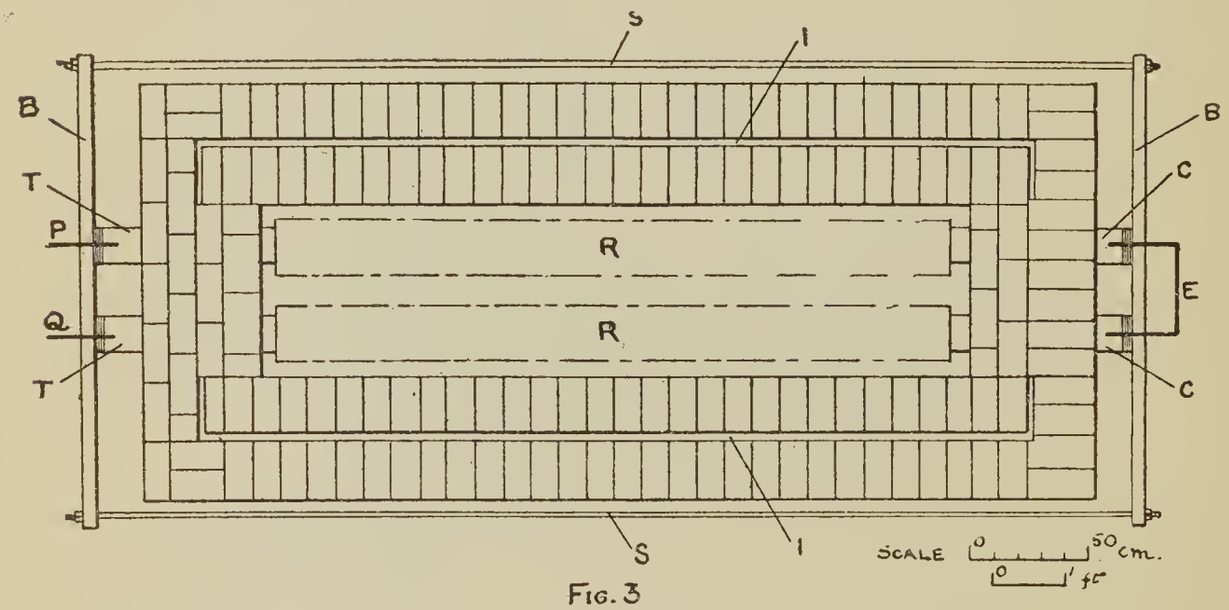

FIG. 3

plates in each section of the resistor. The dimensions of the plates were as follows:

Length at top	405	mm.	(16 inches)
Length at bottom	255	"	(10 ")
Width	165	"	(6.5 ")

When cold, the resistor had a resistance of 0.200 ohm, and when running at the full capacity of 150 kilowatts and with a temperature in the furnace of 1400° C., the resistance was 0.0375 ohm. Now, if the resistance of the carbon itself is calculated, it is found to be only 0.00064 ohm, consequently 98 percent of the total resistance is due to the contacts between plates.

In order to run a furnace of this kind, it is necessary to have

means by which a variable voltage can be applied to the terminals of the furnace. If the current is supplied at high voltage and has to be transformed, there can be no doubt that the most satisfactory electrical apparatus is something in the nature of an induction regulator, which permits of a continuous variation of voltage over a considerable range; but satisfactory results may also be obtained with a transformer from which several taps are brought out from the primary coil, so that the secondary voltage can be changed in a series of steps. Both for the furnaces built at Hohenlohehütte and those in the FitzGerald and Bennie Laboratories at Niagara Falls, transformers built for us by the Pittsburg Transformer Company are used with great success. These transformers have a capacity of 150 kilowatts, and have

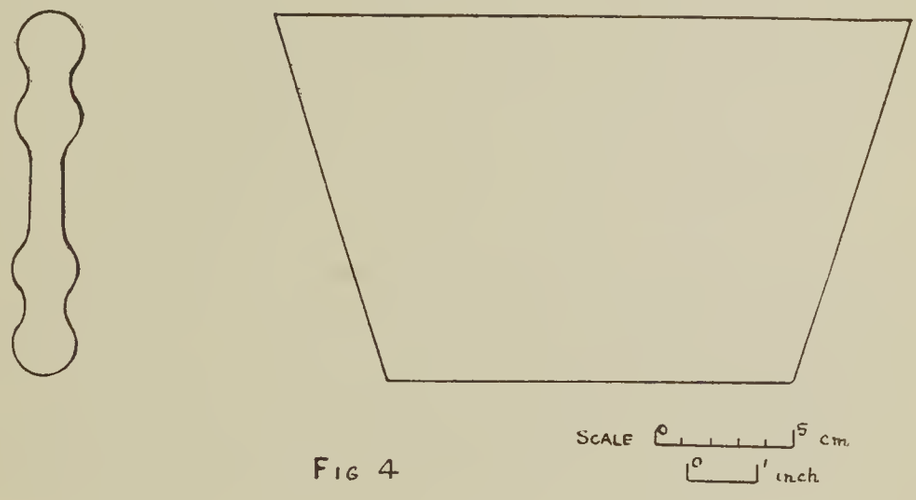

FIG 4

22 taps brought out from the primary coils. Leads are brought out from the two secondary coils and go to a switch, so arranged that the coils may be connected either in series or parallel. When all the turns of the primary coils are in circuit, the e. m. f. at the terminals of the secondary coils is 50 volts. Then, as the turns are cut out of the primary coils, the e. m. f. at the terminals of the secondaries is increased in steps of 2.5 volts until a maximum e. m. f. of 100 volts is obtained. By this arrangement there is obtained at the terminals of the furnace, voltages of 50 to 100 in 2.5-volt steps, and of 100 to 200 in 5-volt steps.

When the furnace described above is to be used with an oxidizing atmosphere in the melting chamber, the resistor is in a closed compartment, the floor of which is made of recrystallized carborundum plates or graphite plates coated with recrystallized carborundum to prevent them from burning. Fig. 6 is a photo-

graph, looking down into one of these furnaces, and shows the two terminals and a few of the plates which form the bottom of the resistor chamber in place. The photograph also shows one section of the resistor mounted in clamps and ready to be put into the furnace.

Some anxiety was felt in regard to this design, for a rather obvious criticism was that there would be a considerable loss of heat in passing from the resistor chamber to the melting chamber. In other words, the thermal conductance of the side walls and top of the resistor chamber would approach that of the bottom of the resistor chamber in spite of the high conductivity of the

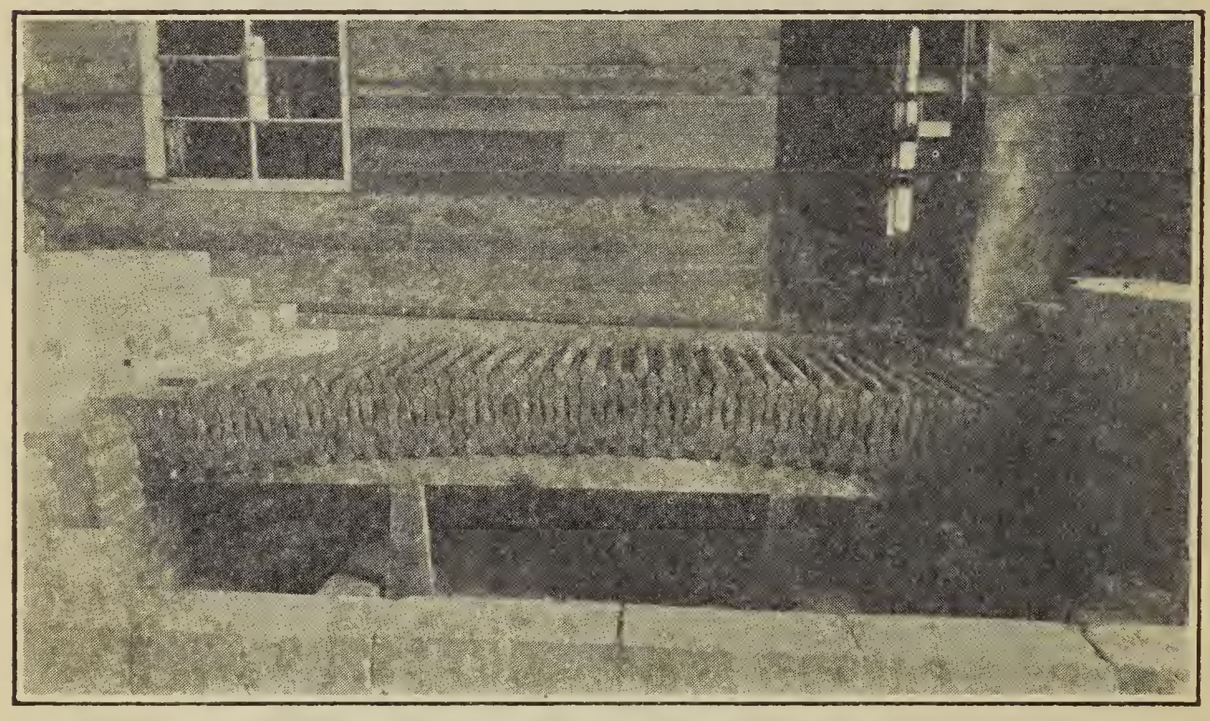

FIG. 5. The Resistor.

latter. Fortunately these fears proved to be groundless, for, in the case of the furnace shown in Fig. 6, it was found that with a temperature of 1160° in the resistor chamber there was a temperature of 1090° in the melting chamber, and with a temperature of 1400° in the resistor chamber, a temperature of 1290° in the melting chamber. In this particular furnace the heat insulation of the side walls and top of the furnace was not good, owing apparently to the high conductivity of the refractories employed, so the thermal conductance was higher than it should have been.

It is believed that this furnace will find various useful appli-

cations. It apparently gives excellent results in the melting of copper, brass, aluminum, etc. It has not yet been tried for glass melting, but it is thought it will do this work well.

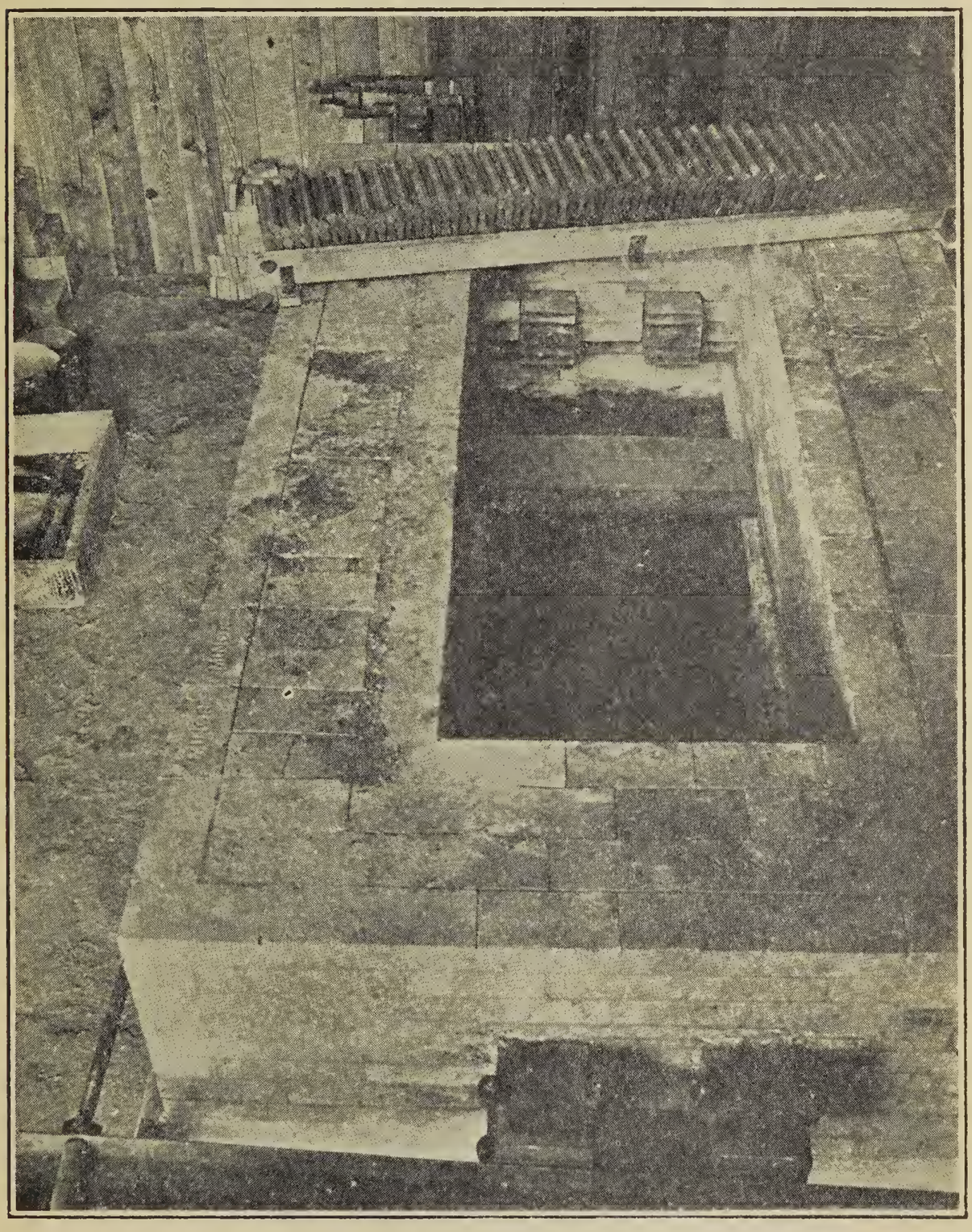

Fig. 6. Interior of Furnace, dismantled.

Finally, it must be pointed out that the design of this furnace is such that it lends itself readily to the combination of fuel and electric heating. Experiments in this direction have been car-

ried on, and it may be said that the results are highly satisfactory, but as these are not yet sufficiently advanced, any discussion thereof must be reserved for another paper.

FitzGerald and Bennie Laboratories,
Niagara Falls, New York.

DISCUSSION.

DR. W. R. WHITNEY: Has Mr. FitzGerald any data on the life of carborundum-coated graphite, when heated and exposed to the air?

MR. F. A. J. FITZGERALD: No; I have not any data on that. I have had these carborundum-coated plates running for about ten days or two weeks at the longest. As regards the plates made of re-crystallized carborundum, we have had some of them in continuous operation for a year.

MR. C. F. CARRIER: I have recently seen described, but cannot tell exactly where, an electric furnace for heating iron bars which consisted simply of a number of arcs beneath the roof, and heating from the arcs by radiation. What is the advantage, as compared with this arc-type, of having the resistance heater overhead? It would seem that the direct utilization of the heat of the arc by radiation downward would be more efficient than the use of the resistor, unless there is some particular advantage in the resistor, or some particular disadvantage in the arc—I would like the point cleared up.

MR. FITZGERALD: The disadvantage in using an arc as suggested, is that the arc has a temperature much higher than is needed for certain kinds of work.

DR. WHITNEY: With arc heating you require mechanical devices for regulating the electrodes. There is no mechanical device required in the resistance furnace at all.

A paper presented at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 6, 1911, President Wm. H. Walker in the Chair.

AN ELECTRIC FURNACE FOR HEATING BARS AND BILLETS.

By Thaddeus F. Baily.

The possibility of an electric furnace for heating metal without melting it was suggested by the writer some years ago on noting the very wasteful and thermally inefficient oil-fired furnaces for heating forging stock used in a comparatively modern plant in northern Ohio.

A calculation of the thermal efficiency of the furnaces in question, which were said to be of the most modern construction, showed that less than 4 percent of the heat value of the fuel was delivered into the steel. The technical press and various publications at the time contained a number of descriptions and tests of electrical furnaces then in use in the chemical industry, and also of furnaces for melting and refining steel. The thermal efficiency of these furnaces was given at from 40 to 80 percent, and it was at once apparent that if a thermal efficiency of even 40 percent could be realized in a furnace for heating stock such as was heated in oil furnaces at a thermal efficiency of only 4 percent, that a very considerable loss could be allowed in the means for converting the heat value of any fuel into electrical energy for use in electric heating furnaces, and still effect a saving.

Taking even a case where the least efficient of the modern prime movers—the non-condensing steam engine—was used for generating power, allowing a net thermal efficiency of 5 percent for conversion of the heat value of the fuel into electrical energy, and assuming an electrical furnace efficiency of 40 percent, the net over-all efficiency for the entire heating equipment would be 2 percent. The fuel for creating the steam, however, would cost only one-third as much per heat unit as would the fuel oil for oil furnaces. The commercial efficiency, then, as far as cost of fuel alone was concerned, would be 33⅓ percent in favor

of the electric equipment, in spite of the low efficiency of the steam engine. Considering steam engine—low pressure turbine units, or gas engine driven units in place of the steam engine unit above considered, the probable efficiencies of electrical furnace equipments seemed favorable enough to deserve a place in the industry, while in plants where there was a large supply of exhaust steam available, as is the case in the majority of forge plants, electric energy could be so cheaply produced by means of the low-pressure turbine that no type of direct-fired furnace

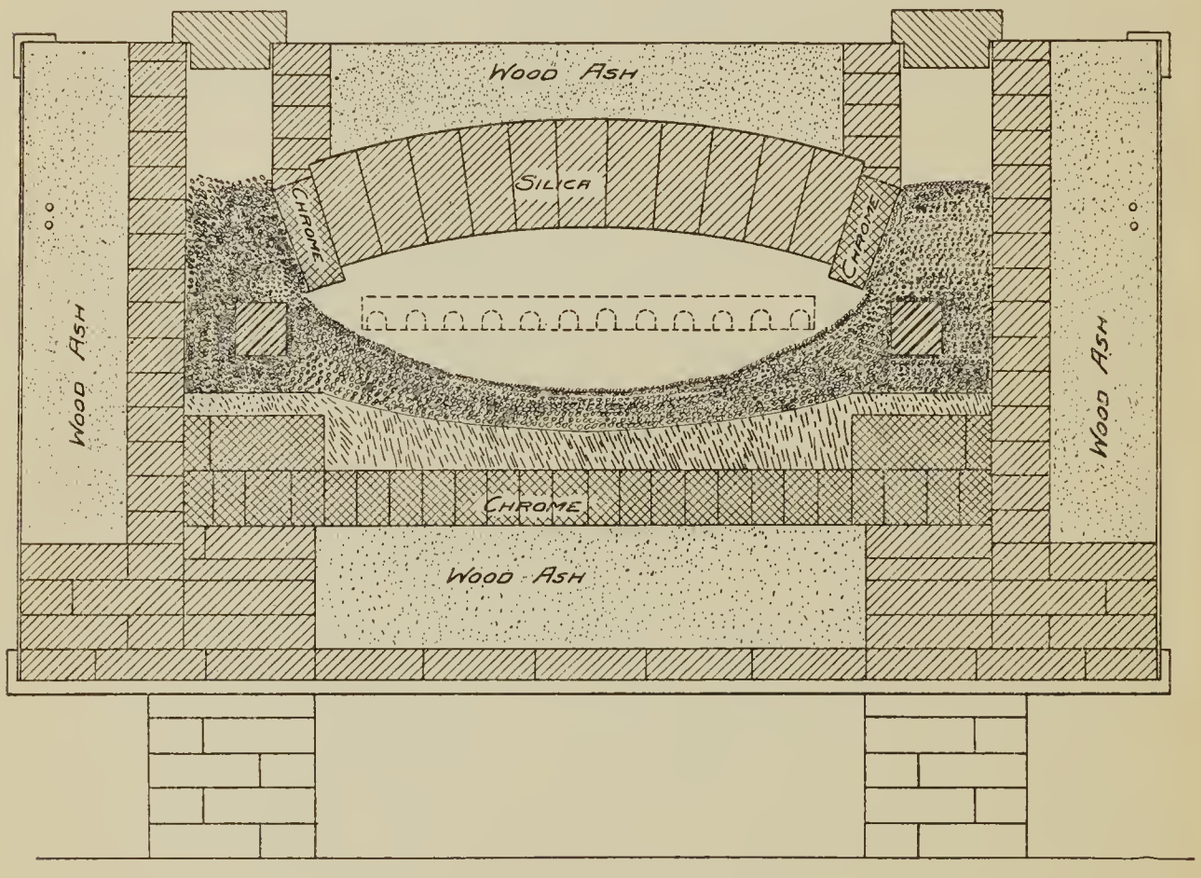

Fig. 1. Vertical, right-left section.

could hope to compete with such equipment in cost of heating. The only question, then, seemed to be whether an electric heating-furnace could be designed to successfully heat metal at thermal efficiencies above a given limit.

The greatest difficulties encountered in the operation of the first experimental furnaces were due largely to lack of sufficient electric current and control devices. Suitable equipment was, however, obtained by installing the 120 kw. generator and transformer equipment mentioned later at the plant of the Transue & Williams Co., Alliance, Ohio, which company very generously sup-

plied the power for driving the generator from their gas engine for all the runs on the furnace.

The following is a description of the furnace evolved out of the experiments commenced over four years ago. Reference may be made to Fig. 1, a right-left section; to Fig. 2, a front-back middle section; and to Fig. 3, sectional plan of the furnace.

The furnace is of the resistance type, and consists essentially of two carbon electrodes, spaced from each other, and an intermediate resistance body of a carbonaceous composition in which the heat is

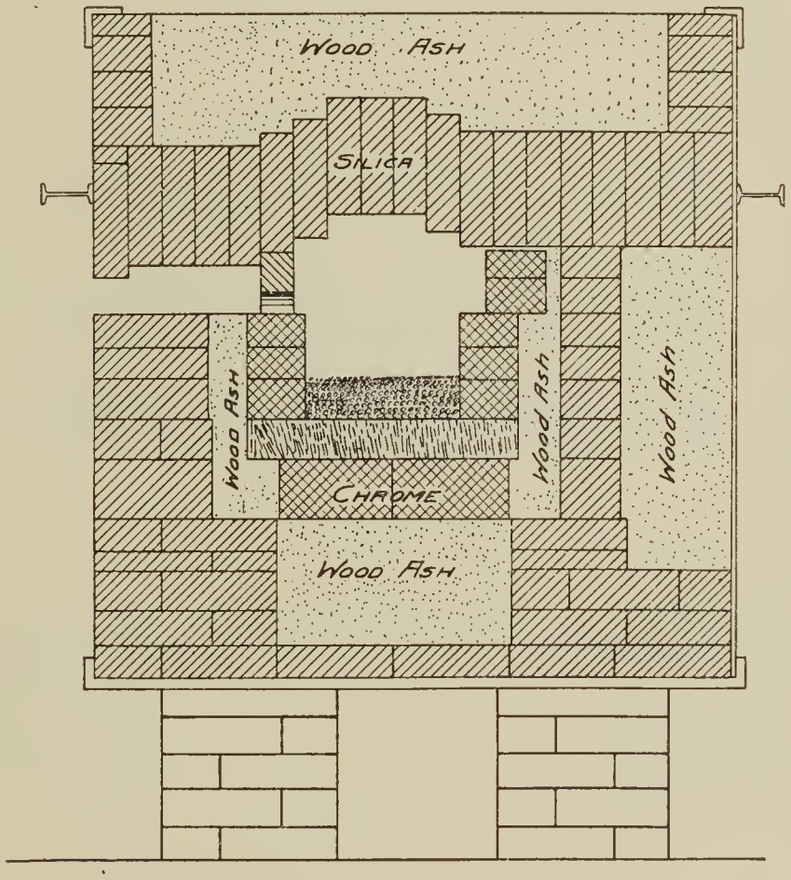

Fig. 2. Vertical, front-back, middle section.

generated. In the space directly above the resistance material and directly under the roof of the furnace is placed the metal to be heated, a ledge at the rear of the furnace and one at the opening supporting the bars or billets as the case may be. The electrodes enter the furnace through the rear wall, and are placed slightly convergent, so that the path of the electric current will be shorter from electrode to electrode at the front of the furnace than at the back. This arrangement compensates for the cooling effect, which is greater in the front of the furnace on account of the opening and the charging of the cold material. The elec-

trodes entering the furnace from the rear present comparatively large contact surfaces to the resistance material, without the use of special electrode sections. The electrodes are also placed in a plane above the resistance material, which throws the shortest path for the electric current in the upper part of the resistance body and nearest the metal. This is a feature that seems almost indispensable to the successful operation of a furnace of this character, since in the furnaces constructed without this feature the cooling of the upper part of the resistance body by the cold

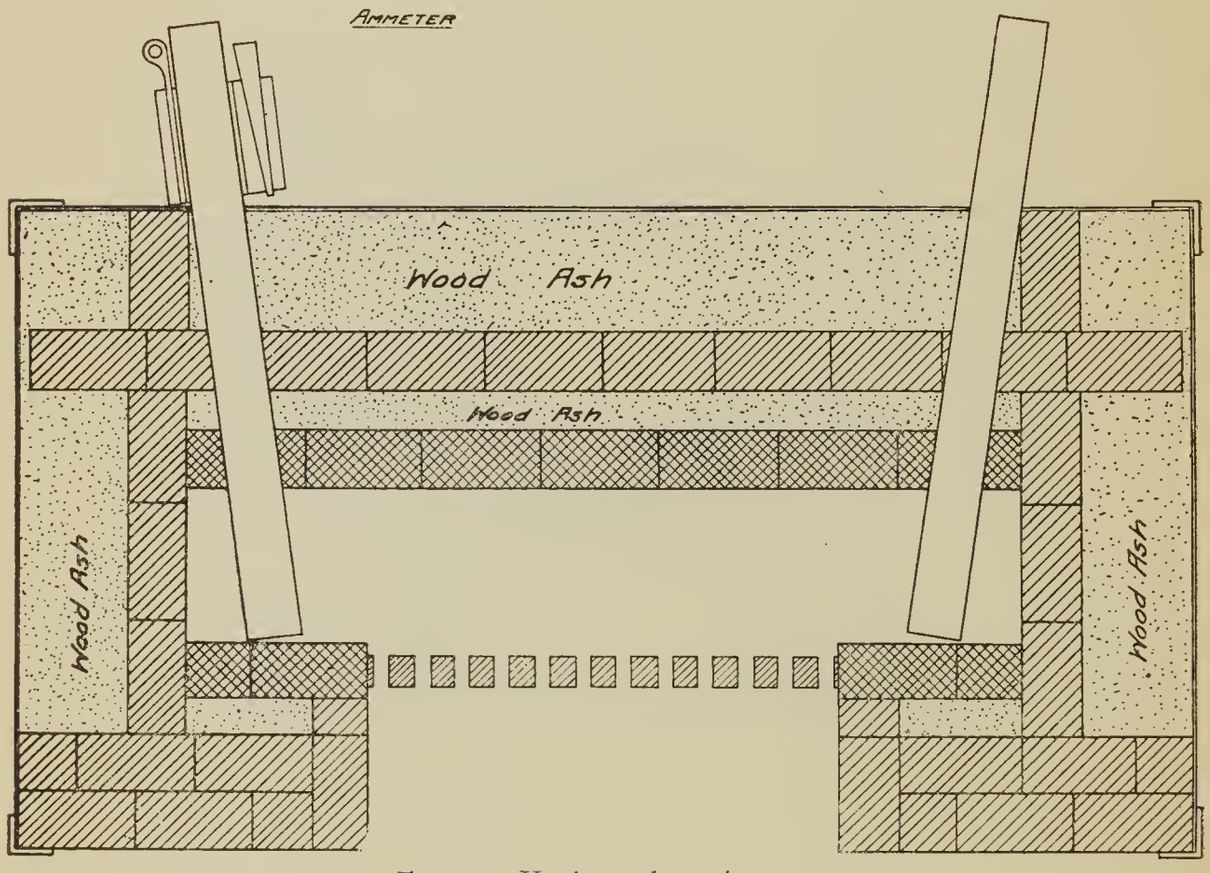

FIG. 3. Horizontal section.

steel caused the electric current to take a lower path, in which portion of the body the temperature became very high and melted out the bottom linings and the bottom of the furnace itself, and at the same time did not maintain the heating chamber at a temperature high enough to heat the metal.

The resistance material is composed of coke or coal. Crushed foundry coke passing over a 0.25-inch (6 mm.) ring and through a 0.37-inch (9 mm.) ring giving the most satisfactory and uniform results. For a 40-kw. furnace, heating 150 pounds (69 kg.) of metal per hour, the distance between electrodes should be 36 inches (90 cm.) and the cross-sectional area about 24 sq. in. (150 sq.

cm.). To maintain an electrical input of 40 kw., a voltage of 200 would be required with a coke resistance body; if the body is composed of coal, the voltage should be about 150 volts. It is extremely difficult to determine the effective cross-sectional area of the material through which the electric current passes, as at working temperatures the lining materials become almost as good conductors of electricity as the resistance material itself. The resistance body as it approaches the electrodes has a very greatly increased cross-section, so as to provide a better contact with the electrodes, prevent undue heating at the point of contact, and prevent, to as great an extent as possible, the dissipation of heat through resistance to the passage of the current except at that part of the resistance body directly under the metal. Thus in a way these increased cross-sections perform the mission of electrodes, as they conduct the current from the electrodes proper, which are located in a protected part of the furnace, to the part where the transformation into heat is desired, and they do this without any considerable heat being generated in these portions themselves.

The most serviceable lining material so far obtained is made of chrome brick and chrome ore, and while a certain reducing action takes place between the chrome ore and brick and the carbon of the resistance material, it is not of such nature as to seriously impair its usefulness as a lining material. This chrome lining is carried up to at least one course above the resistance material. The lining is readily accessible for repairs or inspection by removing the three courses of silica brick directly under the furnace opening.

The top of the furnace is composed of silica arch brick, and is 9 inches thick, and clamped from front to back. A row of chrome arch brick is placed at each side of the roof to prevent contact of the silica brick with the carbon in the hoppers above the electrodes.

The sides of the furnace are composed of silica brick and, in the larger furnaces, are incased in a sheet steel frame. Insulating material is placed between the silica brick and the casing.

The furnace base consists of a heavy cast iron plate supported by cast iron legs or brick piers.

The cable terminals are connected with the electrodes by means

of iron sleeves, copper straps and iron wedges. In making the connection, the iron sleeve is placed over the end of the electrode and copper straps placed against the four sides of the electrode. The copper cable terminal is then placed between one of the copper strips and the iron sleeve, and wedges driven in on the opposite side between the strap and sleeve, and a firm contact thus secured. Wedges are then driven in on the other two sides between the copper strips and the sleeve. In this way the current flow is equally distributed on all four sides of the electrode by means of the encircling iron sleeve.

The furnace is controlled by means of a regulating transformer and controller. The transformer gives full rated output at the lowest voltage rating. While hand regulation is usually provided, the regulation may be made automatic at a slight additional cost. A voltage range of from 33 to 50 percent is usually provided, depending on the operating and starting requirements.

Each furnace is provided with a single-panel switchboard having mounted on it a voltmeter, ammeter, watt-hour meter, circuit-breaker and oil switch. The voltmeter and ammeter indicate at all times the conditions in the interior of the furnace, as irregularities are readily noticeable on the instruments. The watt-hour meter enables accurate data to be kept on the current consumption for heating any particular class of work.

The temperatures that may be obtained are limited solely by the electrical input and the temperatures allowable by the refractory linings of the furnace. The temperature usually maintained in a furnace for the rapid heating of stock for automobile forgings is such as to cause the fusion of the ends of the silica brick forming the roof, and is probably not less than 3200° F. (1765° C.). The resistance material, of course, reaches a much higher temperature. When working at the highest temperatures usually met in forge practice, a renewal of the lining of the bottom of the furnace will be required every two to three weeks.

The replacing of the lining or portions of it and the replenishing of the resistance material are the only items that may be classed as renewals, and should not exceed, in furnaces heating 150 pounds of metal per hour, working at the highest temperatures, an average of 20 cents per day for lining material and 5 cents per day for resistance material.

The metal being heated is maintained in a reducing atmosphere, the high temperature carbon resistance material giving off a gas of a reducing nature. The electric furnace is the only furnace built in small units in which both a high temperature and a reducing atmosphere may be maintained. The saving in oxidation loss is very considerable in small furnaces of this character, as the loss from oxidation in the usual combustion furnace is the cause of the loss of a large number of forgings, due to the fact that a piece of stock, having lost a considerable amount of metal by the oxidizing flame of the combustion furnace, does not contain enough metal to fill the dies.

The thermal efficiency of the furnaces varies with the size, the percentage of operation at full capacity and the ruling temperature required. Efficiencies of from 33 to 65 percent may be expected in furnaces with heating capacities of from 120 pounds (55 kg.) per hour to 1,000 pounds (455 kg.) per hour.

Reference was made in the first part of this paper to the experimental furnace installed at the plant of the Transue & Williams Co., and a description of the apparatus and results obtained may be of interest.

The power for driving the generator was supplied by a 12 by 16-inch (30 by 40 cm.) Buckeye four-cylinder twin single-acting gas engine, which not only drove the generator for supplying current to the furnace, but also for driving a portion of the motors in the machine shop, so that only part of the time was sufficient power available for furnace operation. Belted to the fly-wheel of the gas engine was the 120-kw., 2-phase, 440-volt revolving field alternator, only one phase of which was connected up. The leads from this phase were connected with the low-tension terminals of a 37.5-kw., 440 to 2,200-volt transformer. The current was then stepped down by means of a 2,200-220 or 110-volt transformer, the coils on the low-tension side being so connected through a double-throw switch for either series or parallel operation, so that a normal voltage of either 110 or 220 volts could be obtained. The variations between 110 volts and 220 volts on the lower voltage and also on the voltages above 220 were obtained by varying the field of the alternator. By this arrangement a possible voltage range could be obtained of from 90 to 300 volts, which was more than ample

for conditions of operation. Inability to readily obtain a 2,200-volt generator of proper size accounted for the use of the 440-2,200 step-up transformer. From the double-throw switch the current was conducted to the furnace, located in the forge shop, some 75 feet (22 m.) distant.

The instruments mounted on the switchboard consisted of a 150-volt voltmeter and a 600-ampere ammeter, both made by the Westinghouse Electric and Mfg. Co. The voltmeter was so

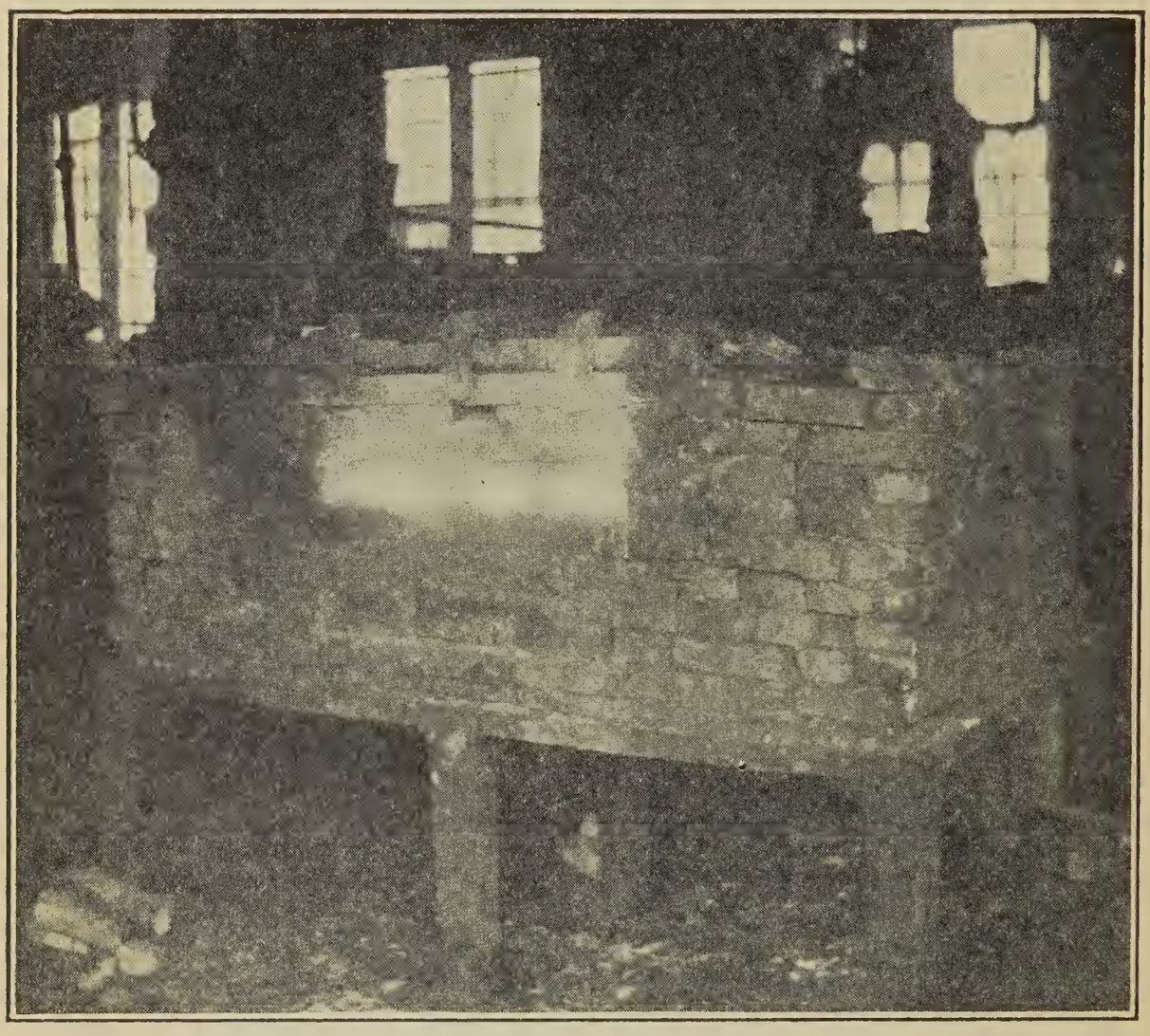

FIG. 4.

connected that when the low-tension coils of the step-down transformer were thrown in parallel, the instrument gave a direct reading, and when in series, the indicated voltage was half the actual voltage.

The furnace was constructed substantially in accordance with the description given in the first part of this paper, except that air spaces were used in place of the insulating material shown in Fig. 2, and it was rated as a 40-kw. unit, having a heating

capacity of 120 pounds (55 kg.) per hour, the heating capacity being rated somewhat lower than the usual practice on account of the high temperature required. Fig. 4 shows the furnace ready for charging; Fig. 5, heating eight 1½ x ⅝-inch (37.5 x 15.6 mm.) bars.

The electrodes were 4 x 4 x 48 inches (10 x 10 x 120 cm.) long, composed of carbon, and were spaced 36 inches (90 cm.) from each other. The cross-sectional area of the resistance mate-

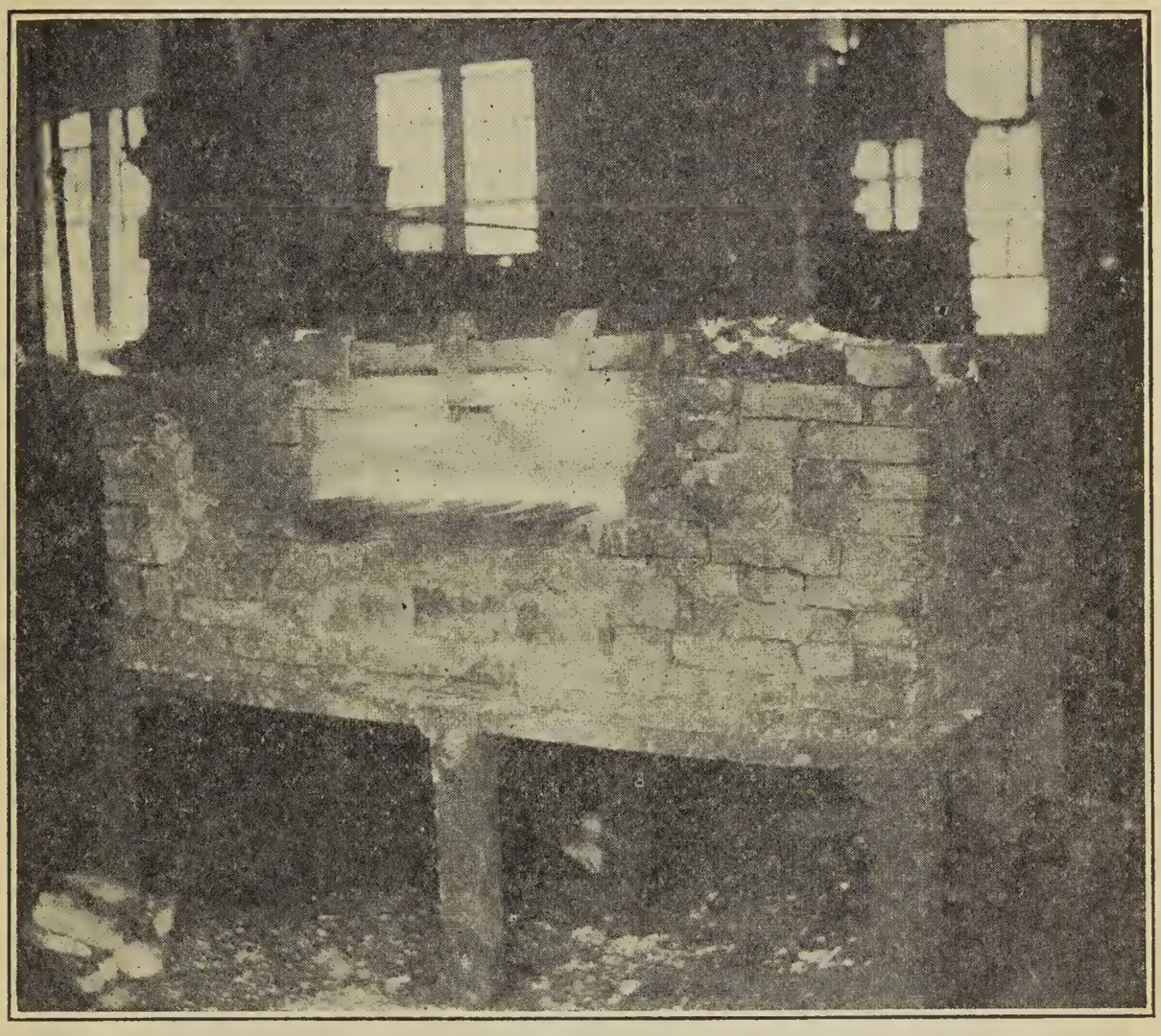

Fig. 5.

rial was approximately 24 square inches (150 sq. cm.). The walls were composed of 9 inches (22.5 cm.) of silica brick, and were of rather loose construction, owing to the numerous changes that were made and to the jar from the hammers in the plant. The runs on the furnace were made under rather unfavorable conditions, since the forgings that were made under the hammer that the furnace supplied were very difficult to make, and unless the metal was very hot, it would not fill out in the dies. Much

delay was also caused by trouble with both the hammer and the dies, any such delay affecting, of course, the amount of metal heated in the furnace.

The stock heated included 1¼-in. (31 mm.) square, 1½ x ⅝-inch (37.5 x 15.6 mm.) flat, 1½ and ⅞-inch (37.5 and 21.9 mm.) round bars in lengths from 22½ inches (56 cm.) to 6 feet (180 cm.) long; 4 to 12-inch (10 to 30 cm.) cuts were taken off at each heating and the bars replaced in the furnace. From 7 to 9 bars were heated at a time.

The current efficiency taken over periods of 9 hours when heating the heavier of the above mentioned stock was from 3 to 3⅓ pounds (1.36 to 1.52 kg.) of metal per kw. hour. Tables 1, 2, 3 and 4 are logs of typical runs of some of the sizes of stock heated.

TABLE I.

Time of Charging	Volts	Amp.	Stock	1st Cut	2d Cut	All Out
9.50	150	270	6 — 1¼″ □ x 132″	10.15	10.25	10.45
10.55	160	260	3 — 1¼″ □ x 66″	11.11	11.15	11.28
12.23	150	270	8 — 1¼″ □ x 180″	12.38	12.44	12.55
1.00	153	260	8 — 1¼″ □ x 180″	1.12	1.20	1.37

TABLE II.

9.25	127	340	8 — 1½″ x ⅝″ x 5′ 10″	9.33	9.38	10.42
10.51	122	350	8 — 1½″ x ⅝″ x 5′ 10″	10.58	11.01	11.19
12.32	128	330	Metal unforged at noon time	12.38	12.41	1.25
1.27	132	330	8 — 1½″ x ⅝″ x 5′ 10″	1.35	1.38	2.44

TABLE III.

1.20	230	180	5 — 1½″ O x 2′ 0″	1.40	1.51	2.07
2.08	230	180	7 — 1½″ O x 2′ 0″	2.30	2.34	3.08
3.17	208	200	7 — 1½″ O x 2′ 0″	3.30	3.36	3.52
3.55	204	200	7 — 1½″ O x 2′ 0″	4.01	4.07	4.29

TABLE IV.

Time of Charging	Volts	Amp.	Stock	1st Cut	2d Cut	All Out
3.55	240	140	8 — ⅞″ O x 27″	4.00	4.02	4.25
4.26	172	150	8 — ⅞″ O x 9″	4.30	4.33	4.36
4.37	252	120	9 — ⅞″ O x 22″	4.40	4.44	4.55
4.57	280	120	8 — ⅞″ O x 9″	5.01	5.04	5.07

A voltage of 250 volts was usually used in starting the furnace in the morning. From one to two hours was usually required to bring the furnace up to temperature. The voltage was then reduced to about 200 volts when using a coke resistance body, or 150 volts for a coal body, which tensions enabled the required electric input to be maintained.

Some of the various linings used before the chrome lining was selected were magnesia, carborundum and silica. The chrome lining, however, gave by far the most satisfactory and uniform service, lasting three weeks without renewal or repair. As only the bottom lining is subjected to very high temperature, it is practically the only part requiring renewal, and as the usual bridge wall used in oil furnaces is not required, that saving compensates for the cost of renewals of the lining of the electric furnace.

The principal advantages of the electric furnace are its high thermal efficiency, its non-oxidizing atmosphere in the furnace chamber at all temperatures, and its freedom from soot, smoke and the hot contaminating gases of the products of combustion.

There seems little reason to doubt that the electric furnace will soon occupy an important place for heating metal such as is now heated in small direct-fired furnaces.

DISCUSSION.

PROF. J. W. RICHARDS: How does Mr. Baily determine the thermal efficiency of the heating?

MR. T. F. BAILY: That is done by assuming that steel heated to a certain temperature, whatever temperature is called for by the work, requires so many heat units per pound of steel. When heating steel bars of standard cross section, we measure the length of each bar, and find the weight per foot. In this way we found the number of heat units that would be required to bring the given number of pounds of metal up to a certain temperature; then we compared that with the number of kilowatts actually consumed as indicated by the meter. The readings were taken every fifteen minutes during a run of nine or ten hours. These

readings, as given in the printed paper, are taken from actual conditions of operation, and were subject to all the troubles incident to hammer operations, the convenience of the men, etc.; in other words the actual conditions in commercial operation.

Prof. Richards: I would remark in that connection that the efficiency obtained was high, considering the way in which the heating had to be done. These bars are heated, as I understand, at one end, with the cold end sticking out of the furnace, and therefore they are treated under the most unfavorable conditions for economically applying electric heat, the heat being radiated from the cold ends of the bars, which must necessarily be kept cold to be handled. To obtain an efficiency of that amount under these conditions is good working.

Mr. Baily: The bars are heated on one end only, then taken out of the furnace, and a piece cut off the end. They are replaced in the furnace, and the operations repeated. Each time, while we had the advantage in time of the second cut, as we call it, nevertheless, we had the loss from radiation of the hot end of the metal while it was out of the furnace having the first cut taken off. Account of this loss would give the furnace a more favorable showing from a thermal efficiency standpoint, than it really makes in our test sheets.

Prof. Richards: I would also call attention to the fact that Mr. Baily makes very effective use in his furnace of the same principle Mr. FitzGerald makes use of; namely, that of getting the resistor hottest next the object to be heated. Mr. Baily provides for the larger part of the current going through the upper part of his resistance material, so the radiating surface is the hottest part of the resistor. The heating effect of the current in any part of a conductor is proportional to the relative conducting power of that part.

Mr. Baily: The resistor is all of the same material. It is simply common coke, crushed to one-quarter inch mesh, and the plan is to make the shortest path across the top. Above the resistor we provide a clear space of from one to four inches, and in this way any part of the resistor that might become excessively hot will distribute its heat and not burn the metal. The temperatures we had to maintain in the furnace I was speaking of were

such that if the metal was left for three or four minutes extra time, the whole end of the heated bar would melt off. It was difficult forging; the dies for it were very deep.

MR. CARL HERING: The method of measuring the efficiency seems to be a fair one, if I understand it correctly, but it depends very greatly on what constant is used for the specific heat of the iron, which may be very indefinite for these high temperatures. This specific heat seems to rise very rapidly with the temperature, and is said to be four times as high at the high temperatures.

MR. BAILY: We use, I think, the figure 0.15, and the various temperatures we worked at corresponded to a heat capacity of about 350 B. t. u., per pound (195 Cal. per kg.), as I remember the figures. These figures are based on an average of some eight or ten tests made in the following manner: A known weight of heated iron was dropped into a bucket of water, and the rise of temperature of the water noted. We had, however, to assume the temperature of the bar in the test, and we got anywhere from 305 to 410. We then assumed about 350 B. t. u. per pound, as the average of the tests we made.

MR. E. A. SPERRY: In measuring the efficiency of the furnace, what account was taken of the heat lost by conduction through the portions of the bars that protrude from the furnace? Was that loss taken into account? Only a very small amount of heat is thus lost, however, much smaller than is generally supposed under such conditions.

MR. F. A. LIDBURY: I should like to ask if any one will be bold enough to define the thermal efficiency of an electric furnace.

PROF. RICHARDS: The ratio of the heat actually used for useful purposes to the heat energy of the current.

MR. LIDBURY: Then according to some figures published by Prof. Richards recently, the efficiency of the Heroult furnace at South Chicago, is *nil*. Metal goes in at a certain temperature and comes out at the same temperature. I don't think a definition of that kind will carry us very far.

MR. H. K. HITCHCOCK: I did not have a chance to read this paper before I came in, but I would like to ask the author if he took into account the heat given up by the oxidation of the coke.

From my experience I would expect that the particles of coke forming the upper part of the bed would ozidize, leaving a film of ash on the outer surface, which would increase the resistance of this upper layer and would tend to force the greater flow of current into the lower part of the bed, instead of having the greater current density along the top, as has been suggested. The increased weight on the lower portion of the coke, as also the increased temperature there, would reduce the resistance of the lower portion of the bed and still further tend to increase the current density in the lower portion.

The oxidation of the coke also would furnish considerable heat, which would tend to modify the calculations of efficiency of the furnace, making it lower than it otherwise would be.

Mr. Baily: In that connection I will say that additional coke was required about every five or six hours. It was simply thrown in, and no ash taken out until we had to re-line the furnace. It accumulated until oftentimes it got up within half an inch of the metal. We then raked it out. As a matter of fact, we were under the impression at one time that it made little difference what kind of resistance material we used, when the furnace was once heated. We got good results at one time without any coke in the body of the furnace whatever—the lining carried it entirely. Under such conditions, at the end of three or four hours, we got arcs all through the bottom lining of the furnace, which necessitated our putting in a coke resistance material again, which promptly remedied the arc trouble in the lining. As far as the ash is concerned, the ash seems to be a fair conductor of electricity at such temperatures as we attained in the bottom lining. I estimate these were about 4000° F. (2200° C.), as at various times we used magnesite, chrome and carborundum lining, all of which were more or less fused. In answer to Mr. Sperry's question regarding the loss through the bars, I think the point is well taken. I never made any calculation of what went through the bars, but I think that we always utilize at least 95 percent of the heat that passes into the bars, because the whole bar has to be heated to the maximum temperature and any such heating as mentioned can be classed as usefully applied and not as a loss, as in the case of the heat traversing the wall of a furnace.

A paper read at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 6, 1911, President Wm. H. Walker in the Chair.

A REPLACEABLE UNIT SYSTEM OF ELECTRIC HEATING APPARATUS.

By Milton M. Kohn.

It gives me great pleasure to read my first paper on this subject before the members of the Electrochemical Society. The main object of this paper is to show the difference in construction as well as the results obtained by the multiple unit system, as compared with the solid or integral method of building heating devices. No specific data will be given here, as this may form a subject for a future paper.

The chief reason for the limited use of electric heating apparatus is, in my opinion, the certainty of the device burning out sooner or later, no matter how carefully it may be used. This is an inherent fault in all electrical apparatus, but is experienced more frequently in electrical heating devices because of the cumulative effect of the heat, which, unless taken care of by some heat-absorbing article, will sooner or later cause a burn-out.

The replaceable unit system has been designed to give to electric heat-producing devices a construction possessing all of the advantages of other kinds of heaters as well as some not to be found elsewhere. Any device, no matter what its character or purpose may be, should be so constructed that it can be repaired and parts replaced by an unskilled operator, and this without any excessive cost. This statement may appear a little broad on its face, but if the article is to be used universally, it must, generally speaking, comply with this requirement.

The existing method of constructing an electric furnace is, as we already know, to take the chamber to be heated, such as I show here, which is made of some refractory material, and wind it with the necessary resistor, which is held in place mechanically by cementing it or by other means, and then place this in a case of metal, the space between being filled up with heat-resisting

material and the ends closed. This makes a structure which, in case of a burn-out, requires complete dismantling, in order to get at the burnt-out resistor.

Without going further into details, it can be seen that, because of this method of construction, the cost of repairing a burnt-out furnace is a large percentage of the first cost, besides which, in view of the fact that the resistor is on the outside of the chamber to be heated, any desired temperature on the inside of the chamber will necessarily mean a much higher temperature on the resistor proper, owing to the more or less imperfect heat conductivity of the chamber itself. This will immediately

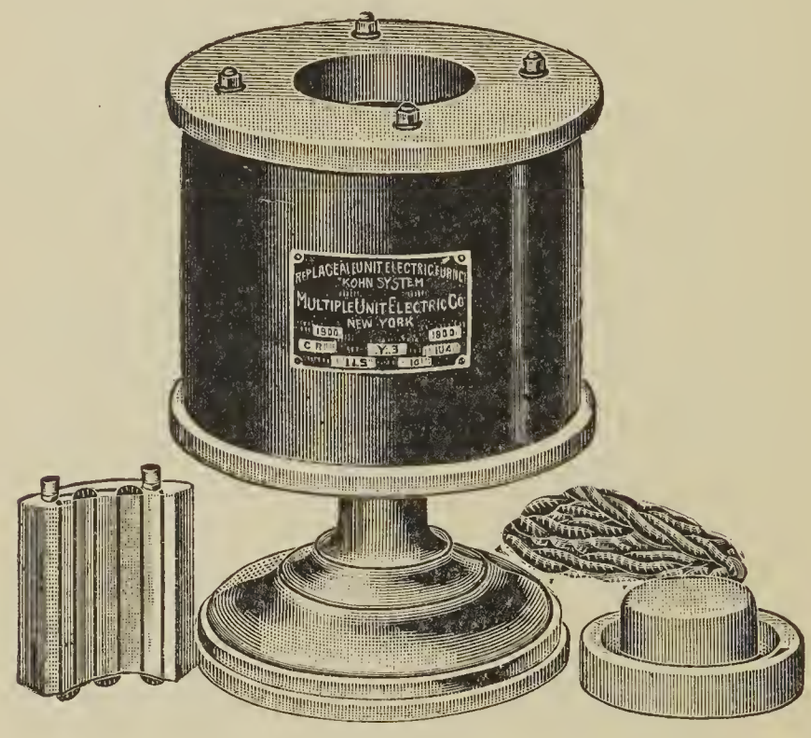

FIG. 1. Crucible Furnace.

reduce the efficiency at any desired temperature, beside which, if the furnace is run at its maximum temperature, the resistor is working at a temperature which is very near its danger point.

The system employed by the Multiple Unit Electric Co., of New York City, consists of a method by which the heating elements are used in a structure which is separate and distinct from them. The essential points are the replaceable units, used in multiples of two, by means of which a burned-out or otherwise damaged section can be almost instantaneously replaced by the operator and at a cost which, compared with the present method of repairing a burnt-out electric heating device, is nominal. The

disadvantages already mentioned, which are found in the existing electric heating devices, have, we believe, been fairly well overcome, and to this end the construction is radically different in the following respects: In the first place, there is no chamber used, nor is there one required, except for extremely fine and delicate work, the units themselves forming the chamber. In the second place, the resistor is placed in units which have open slots, so that while the resistor is protected from mechanical and electrical injury which might result from the work which is placed in the furnace, it is still in such a position as to give off its maximum heat to the work, thereby giving very greatly increased efficiency

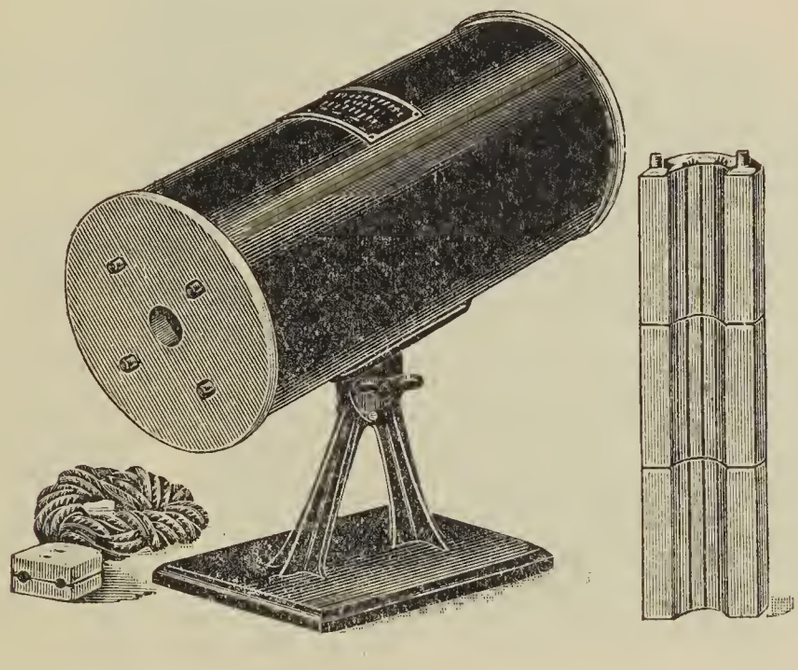

FIG. 2. Combustion Furnace.

over the usual construction. With this construction it is possible to maintain a chamber temperature of from one to two hundred degrees higher than with furnaces of the older types without raising the working temperature of the heating medium.

To recapitulate, the replaceable unit system has the following advantages: Flexibility of construction, replaceability of the damaged portion of a heating device without disturbing any other part, ease and rapidity of replacement, very high efficiency, very low maintenance cost, and general adaptability to any and all forms of electric heating apparatus.

A few examples of the great adaptability of this method of construction may be of interest.

In certain industrial work, such as burning color on china, glass and similar material, there are pieces, such as very thin plates, placques and other fragile shapes, where the heating should not be uniform because of differences in cross-section. In other words, the same heat applied to the very thin, almost knife edges of such work will almost certainly burn or melt the color off it, whereas that portion which is the thickest can safely stand a higher temperature. By the unit system of construction, it can readily be seen that it is a very easy matter to so control the temperature on that portion of the furnace that the narrow or

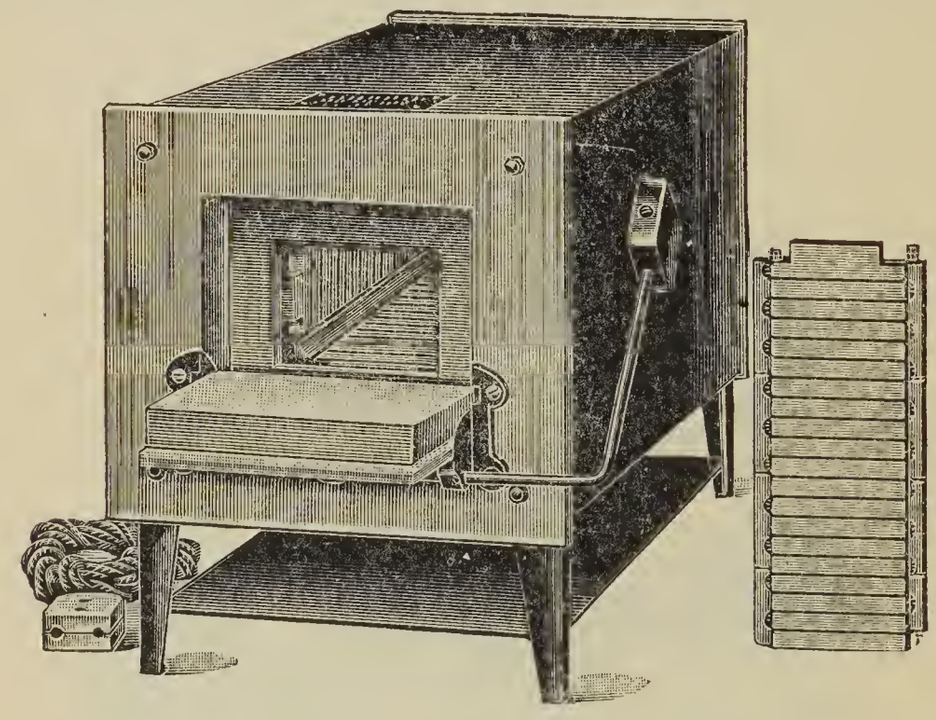

FIG. 3. Muffle Furnace.

thin edges of the work can be heated very much slower or at a lower temperature, if desired, than the thick or body portion.

Again, in some laboratory work for the heating of various liquids, gases, etc., it is sometimes desirable to have the heating only on one side of the receptacle, which may be a tube, flask or any other differently shaped vessel, for the purpose of watching the work while it is being heated. To this end we would employ either a standard unit or a special one built for the particular work in question, which can furnish just the proper degree of heat and at the exact spot where it is wanted.

Another example would be afforded by cases where it is desirable to have what is known as a progressive heat. That is to

say, that the heat should start very gradually at one end and increase by successive stages up to the maximum. This can also very easily be done by using a unit of the required shape and length and so placing the convolutions of the heating medium that the heat will be progressive or gradual as required.

Again, by the unit system of construction, the heat can be made absolutely uniform throughout the entire structure, or by various methods of connecting the units with and without resistance, which latter can be a part of the unit, a separate resistance in the furnace proper, or an external resistance, or a combination

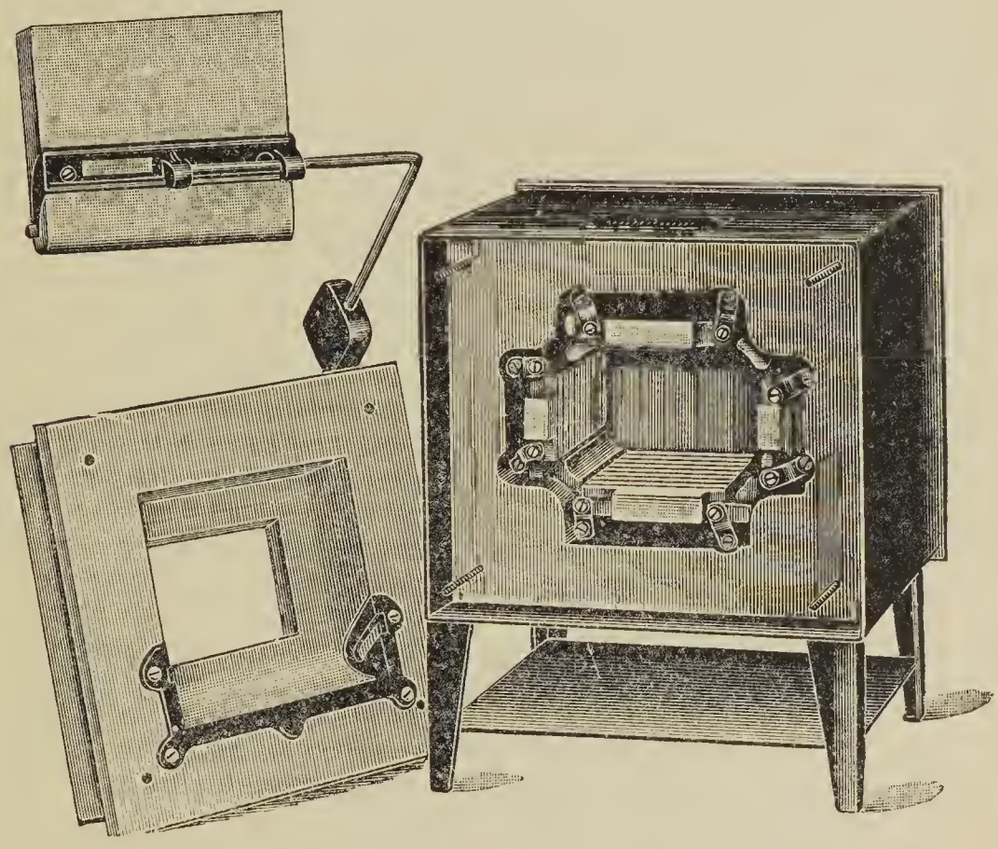

FIG. 4. Muffle Furnace. Front and Door Removed.

of all three of them together, the heat control can be made as gradual as may be required for the most delicate work. I believe, however, that the few instances just given will explain the possibilities of the system.

With regard to adaptability for making special sizes and shapes of heating devices, the system, as already mentioned, has the utmost flexibility. If we would take as an example a muffle type of furnace, such as is shown here, it is seen that the housing or body consists of a number of sections of refractory material; these are formed to make the desired shape, four of them

generally being in a layer and possibly three layers being required to make a standard length of furnace. If it is desired to increase the length of the furnace, all that is necessary is to increase the number of layers so that there is no limit to the length, except that caused by mechanical strength. The units which fit into this furnace are made in the same way; additional lengths can be added so as to make the required length.

With reference to increasing the cross-section of a furnace of this character, it should also be understood that all that is necessary is to insert between the corner pieces which make up the housing or support for the units, a distance piece of the required dimension, by means of which the cross-section can be indefinitely increased, the limitation, of course, being, as before stated, mechanical. The units are increased in the same manner by inserting a special-shaped distance piece which will have the same cross-section as the unit with which it is to be used.

If a unit burns out, in order to ascertain which is the burnt-out unit without removing all of them from the furnace, we use a test plug, which very quickly tells us. Those which are perfect will cause the lamp, which is part of this test plug and which is in series with each unit, to burn, but the burnt-out unit, being open-circuited, will not make the lamp light, and, therefore, we need look no further. This burnt-out unit is removed by unscrewing two nuts and sliding it out, and then replacing it by a new one, and screwing on the two nuts just mentioned, makes the necessary electrical connection. On closing the switch the furnace is again in perfect shape to continue its work.

It makes no difference what the size or the shape of the furnace may be, the burnt-out units are all replaced in the same manner and with the same ease.

For laboratory use, particularly in colleges, a great many professors are desirous of building their own furnaces and winding them with platinum in order to obtain higher heats than can be furnished by base metal resistors. Here again this unit system is exceptionally well adapted for the work. If the safe working temperature is 1100° C. (2000° F.) the furnace will stand a temperature for a short time of, say, 10 percent higher. When this is necessary for a special experiment, the extra temperature can be easily obtained by increasing the current, but, of

course, with the probability of burning out the medium. In this case it can be quickly, in fact, almost instantly, repaired, without taking the furnace apart and at a cost that I know will appeal to the average college professor. Compare this feature with the solid or integral type of construction.

Again, if it is desired to use platinum to obtain higher heats than can be obtained by a base metal resistor, it is only necessary to remove the base metal and rewind with the necessary amount of platinum. If the platinum wire should burn out, it is only necessary to withdraw the burnt-out unit, and as the wire is exposed and can easily be reached with a pair of pliers, and is non-oxidizable, the twisting together of the open ends will quickly put the furnace in working condition again. In chemical operations where delay is sometimes a very serious factor, this would be found particularly useful.

Again referring to laboratory uses, hot plates for sand baths, etc., can be made of any size or shape and to give any desired temperature and any heat control by a simple combination of standard sizes of units and different combinations of circuits.

For domestic use it can be seen that this type of construction has an unlimited field. A few instances will illustrate this. If we wish to take the chill off a room or chamber, a number of these units of any desired size can be supported on the necessary insulating plate and hung on the wall or placed on the floor or any place where it is desired to obtain the heat. If it is to be used for cooking purposes, a similar type of construction can be used.

Another feature about this system especially for laboratory or domestic use is that by means of units which are wound for the various standard voltages, it is not necessary to have separate complete furnaces, but only an extra set of units, so that where a heater has been purchased to operate on a 110-volt circuit, the purchase of an extra set of units wound for a 220-volt circuit will enable the same device to be used on the higher voltage, everything else remaining the same as before. This is a feature that will appeal more to the merchant or jobber who may handle these devices, as he is not compelled to purchase a number of them for different voltages, but can simply stock up with enough units of the different voltages that may be called for.

Before closing, I wish to take this opportunity of publicly acknowledging my indebtedness to Mr. J. F. D. Hoge, who has been of assistance to me in the developing and construction of this system.

DISCUSSION.

DR. W. R. WHITNEY: What kind of wire is used?

MR. M. M. KOHN: It is a special wire. I am very sorry I have to give such indefinite information, but nothing more definite can be said just now.

DR. WHITNEY: A high resistance wire?

MR. KOHN: Yes.

DR. HARRISON E. PATTEN: This paper is very interesting to me, especially as I tried last fall to cut down the heat in our laboratories in the Bureau of Soils, at Washington. I was told they had at the Bureau of Standards electric furnaces for organic combustion which would work, but found that all were out of use; most of the platinum had become crystalline, or had melted or even partly vaporized. They had tried "nichrome" wire, but it burned out. Mr. Cain is working on a furnace using nitrogen around the resistance wire. I thought it might do to use cheap replaceable units and let them burn out. So I tried it, using this nichrome wire of different gauge depending on the effect desired, and using magnesite mixed with asbestos as the furnace packing. It is not a very handy material compared to what is used here, I mean permanent use; but where you want to throw the burned-out units away it is very convenient, because you can get a large bag of it for $4, put it together with water, use asbestos board with sodium silicate binder, and make units in any size you want, in a tin-can as a little mould, and these units can be made in quantities for from thirty to thirty-five cents apiece. I know that the furnace I used did not cost over fifty cents, and for a larger furnace I do not think the construction would cost much over fifty cents.

These units were not non-inductively wound and, of course, if

you had magnetic substances in the furnace you would have considerable trouble, but they worked well enough for what I wanted.

MR. KOHN: If I understood your remarks, you said you had good success in making units out of asbestos boards, combined with silicate of sodium. At what temperature were they used?

DR. PATTEN: I did not measure the temperature. It was sufficient for the ordinary organic combustion.

MR. KOHN: That would be an average of 1,000°C.

DR. PATTEN: Yes. I fused sodium dry carbonate in it with no addition of potassium carbonate. You can start one of these little furnaces going inside of fifteen minutes, and after you get it going you can make an ordinary sodium carbonate fusion in platinum in six minutes. You can take a piece of hard glass tubing and get it up to the flowing point in that time.

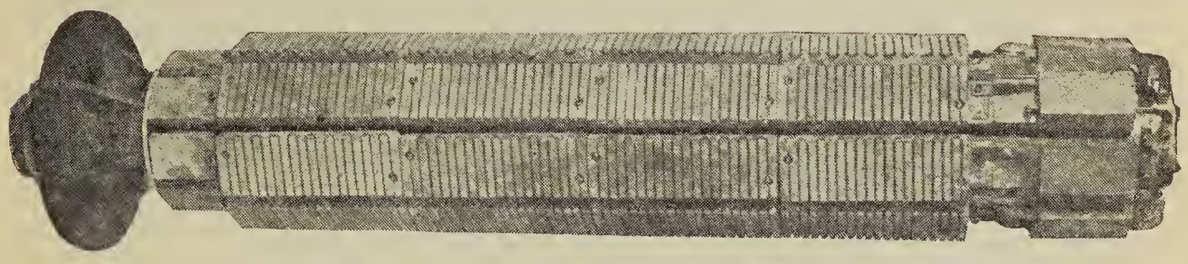

FIG. 5. Roll-Heating Furnace Resistor.

MR. KOHN: How long do the units last at these temperatures?

DR. PATTEN: I ran some of them about five days, seven or eight hours each day. I have not had any of them burn out yet.

MR. KOHN: I think you will find that is about the limit of their life.

DR. PATTEN: That is what I expected. I think it would be a commercial proposition to pay fifty cents for such a furnace and throw it away when we get through with it.

MR. KOHN: I have here on the table another furnace built on the tubular form of construction, or what is known as a combustion furnace, the only difference being that it has a very large opening and is much longer than the standard furnace. They are built stationary, revolving and tilting, and used for hardening small springs in bulk, blueing screws and similar work. This

particular furnace has been made for the purpose of this demonstration to show the manner in which variable temperatures are obtained. There are four units in the furnace, each one of which is separately controlled with or without resistance, and by means of the separate switches the heat can be obtained on the top or bottom, or both top and bottom, or on either side, or on all sides together. In other words, the heat can be obtained in any portion of the furnace and by means of a resistance the temperature can be made just what is desired at any particular point. We consider this a necessary thing particularly in certain kinds of chemical work. A Thwing recording pyrometer is also in position for the purpose of measuring the variations in temperature in different

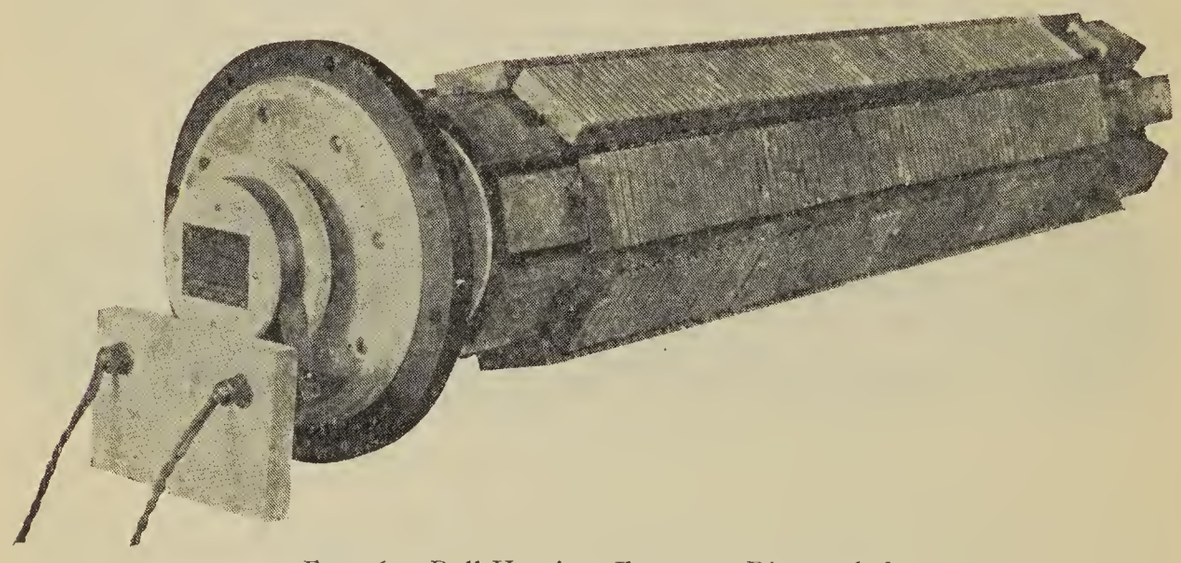

Fig. 6. Roll-Heating Furnace, Dismantled.

portions of the furnace. This pyrometer responds in five seconds to a change of temperature and it requires about five seconds to indicate the temperature after the change is made. It is arranged to point into the furnace, and if any of you care to observe it more in detail after the end of the session, you may do so.

Prof. Joseph W. Richards: I have a small tubular electric furnace like this one; it has a rusty iron coating on the outside. I put on the current and kept it steady until we got a stationary temperature inside, and determined how much current it took. Then I painted the outside with white aluminium paint and let it stand the rest of the afternoon, with sufficient current to get the same stationary temperature again; with the same temperature inside we were using ten percent less power to hold this tempera-

ture than before. The temperature of the outside shell of the furnace, however, as taken with a pyrometer, was thirty degrees higher when painted white, than when rusty, although it was radiating ten percent less energy.

PRESIDENT WALKER: Does Mr. Thwing wish to say anything about the pyrometer?

MR. C. B. THWING: Only to demonstrate the pyrometer. We connect up the recording pyrometer, and now you see it making a record; you can examine it in detail at the close of the session. This is the same recorder as is used on portable instruments, a recording milli-voltmeter. It responds in five seconds to the

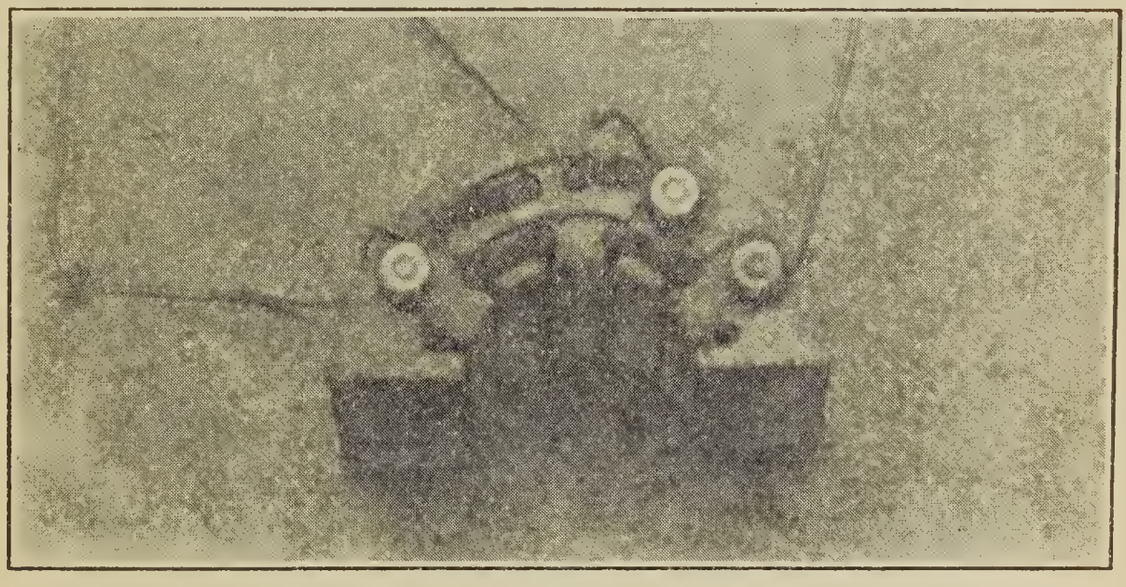

FIG. 7. Resistor With Two Windings.

change of temperature. I have arranged the pyrometer to point into the furnace, to continuously record its temperature as it heats up.

MR. KOHN (*Communicated*): The system, as already mentioned, is applicable for any kind of industrial work. We have built roll heaters 6 feet (180 cm.) long and 14 inches (35 cm.) in diameter, for heating steel rolls for use in textile mills, (see photographs pp. 307, 308) for embossing presses and various other purposes, and find that the replaceable unit system is one which is very favorably received, not only because it is replaceable, but also because the units are, comparatively speaking, small and in sections, the ease with which it is constructed to conform to

special conditions, and also because of its absolute heat control for any purpose whatever.

The last cut shows a unit ordinarily used for a tubular type of furnace in which there art two windings known as the main heating winding and the resistance or auxiliary winding. By means of the double throw switch used therewith it can be seen that by throwing the switch in one position, the main or heating winding has the full current passing through it, giving the maximum heat. By throwing the switch in the opposite direction, the auxiliary winding or resistance is put in series with it, thereby cutting down the heat, with, of course, a corresponding reduction in energy consumption. From this it will be seen that all of the energy put into a heating device arranged this way gives off useful heat, as all of the energy which ordinarily is wasted in an external resistance is here used directly in the heating appliance, thereby giving off its heat inside where it is of use.

A paper read at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 6, 1911, President Wm. H. Walker in the Chair.

THE JOHNSON ELECTRIC ZINC FURNACE.

By Jos. W. Richards.

There exists at present a keen and wide-spread interest in electric zinc smelting. In Europe, the De Laval furnace is in operation on a large scale at Trollhättan, Sweden; another smaller plant is in operation in Norway. Thirty years ago, the Cowles Brothers experimented with an electrically heated retort for smelting zinc ores from a New Mexico zinc copper mine, but they were ahead of their time, as zinc smelters, and no practical zinc process resulted. Their experiments were, however, the progenitors of a great rise in interest in electrothermal smelting processes and of their rapid development in this country during the last two decades of the last century, and thus the search for the electric zinc furnace brought us perhaps even better things.

If the metallurgy of zinc once helped the development of the electric furnace, it seems certainly to be at present true that the electric furnace has now developed to the point where it can help the zinc business, and repay its debt of gratitude by giving to the zinc smelters continuously-working electric zinc furnaces of large capacity.

It is a commonplace remark in metallurgical circles that the metallurgy of zinc has not improved in principle since its start, over a hundred years ago. It has certainly improved in details, such as the introduction of mechanically operated roasters, regenerative gas furnaces, hydraulically-pressed retorts, etc., but it is true that the operative unit of present zinc smelting is still the small retort, with its limited life, thermal inefficiency and corrodibility, operated by costly and crudely applied hand labor. There are now, in the United States, some 100,000 of such retorts in operation, making each only 5,000 pounds of metal per year.

Potentially, the electric furnace starts on a basis far above the old retort, for it can be built in large sizes and it puts the

heat just where it is needed; further, it can be operated continuously, which is far preferable to the intermittent action of the retort. It is quite within the bounds of probability to expect to see, in the future, 500-kilowatt electric zinc furnaces, producing 2,000 tons of metal per year, the equivalent in production capacity of 800 retorts. In such furnaces, the extraction of zinc will be more perfect than in retorts, the metal should be more uniform in quality, the labor charges less, capacity for treating a variety of ores greater, and control of temperature better. The cost of electric power would approximate the cost of the coal used in present practice.

Mr. W. McA. Johnson has worked on this problem since 1903, when he was metallurgist of the Lanyon Zinc Co. He studied

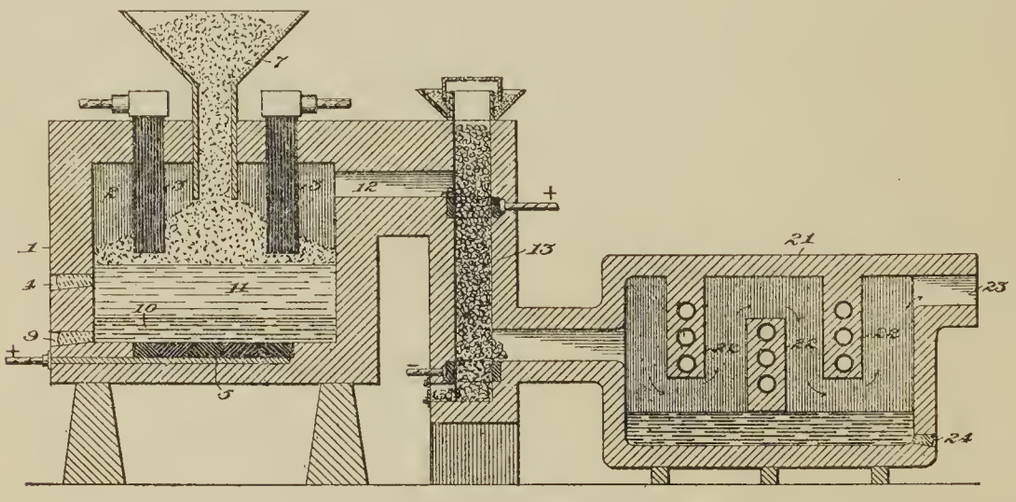

FIG. 1. Section of Small Furnace.

physical chemistry under Professor Nernst at Göttingen, and was electrometallurgist with the Orford Copper Co., under Col. R. M. Thompson. His first experimental work on a large scale was on the lines of treating a charge producing a dry, infusible residue. This was attended by some success, but the main difficulty was met in the condensers, which were unsuited for large-scale, continuous operation. At the meeting of this Society, in the spring of 1907 (these Transactions, **11**, 274), Mr. Johnson stated that the keystone of the electric zinc furnace question was the satisfactory condensation of the zinc. Since 1908, Mr. Johnson has developed an electric furnace for the smelting of zinc-lead-copper ores, intending to produce therefrom condensed zinc, base lead bullion, copper matte, and a fusible thinly-liquid slag.

In this operation, the electric furnace works like a lead-smelting furnace, with reducing conditions strong enough to reduce to vapor all the zinc present, but not strong enough to reduce to the metallic state appreciable quantities of iron from the slag.

The furnace shown in Mr. Johnson's U. S. Patent 964,268, of July 12, 1910, is of the buried arc type. The zinc vapor would, however, be distilled off accompanied by the usual large quantities of carbon dioxide gas, which interferes greatly with the condensation, producing much blue powder. To obviate this, the furnace

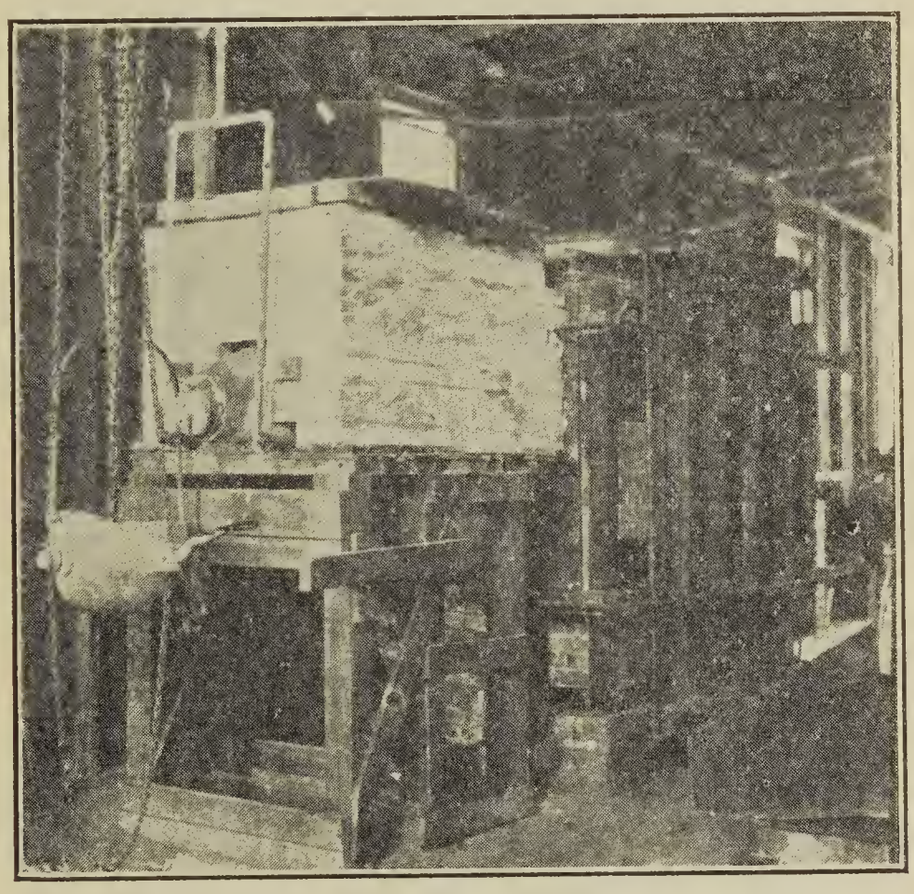

Fig. 2. Small Furnace.

gas and vapor is passed through a carbonaceous filter, kept hot enough by passage of electric current to prevent condensation of zinc within it, and also to cause the reduction of CO^2 in the gas to CO. The mixture of zinc vapor and CO gas then passes into the specially designed condenser, intended to bring the zinc vapor into contact with the surface of liquid zinc, to take away the large quantity of latent heat liberated in the condensation, and to preserve its proper temperature. In usual retort practice 70 to 80 percent of the zinc vapor is condensed to liquid metal, while 20

to 30 percent is caught as 'blue powder,' which must be worked over. Mr. Johnson has obtained results better than these in the condenser attached to his 25 kw. experimental electric furnace. His losses in the liquid slag are also very low, not being over 0.5 percent of the zinc contents of the charge.

A 25 kw. furnace has been operated on this principle. The

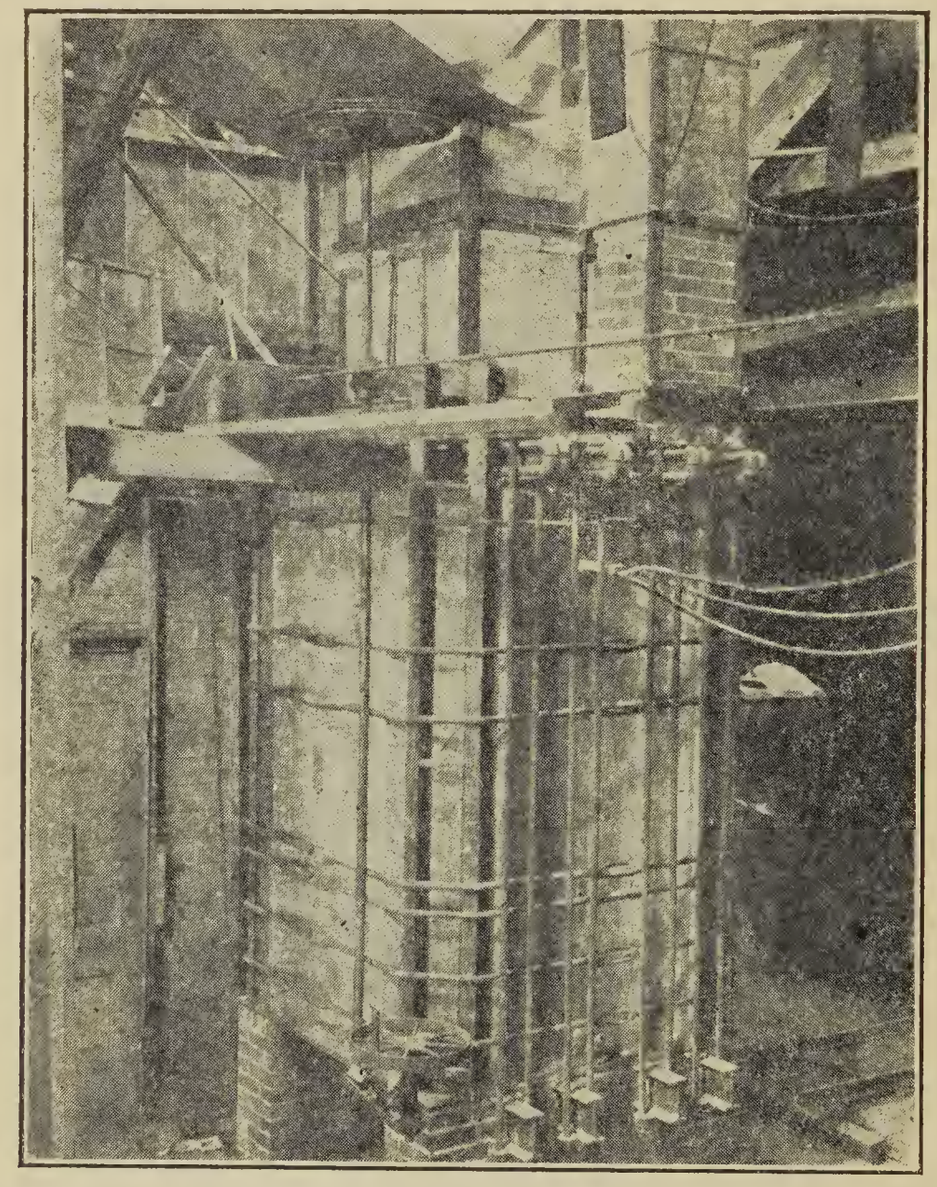

Fig. 3. Larger Furnace.

slag aimed at melted at 1100° to 1175° C., the working temperature of the slag body was 1250° to 1300° C. The gases passed into the condenser at about 850° C. The working zone of the furnace smelts very rapidly. The smelting capacity per cubic foot of smelting zone being 50 times as rapid as in the fire clay zinc retort, and 5 times as fast as in the ordinary lead-smelting

furnace. A larger furnace is being constructed, and will probably meet with less difficulties in the smelting operation, but with more difficulties in the condensing end.

I hope at a later date to be able to present a detailed account of the working of this larger furnace.

Entirely irrespective of the merits of this particular furnace, it is probable that the near future will see the beginning of the abolition of the fire-clay zinc retort in America; we may even say that the new era of electric zinc smelting has dawned. The electric zinc furnace will be another prominent feature of this rapidly progressing age of electrometallurgy.

DISCUSSION.

MR. A. L. J. QUENEAU: What temperature is obtained inside the furnace in the working zone, that is, in the smelting zone?

PROF. J. W. RICHARDS: The temperature in the smelting zone is probably quite high, but the power is regulated so that the zinc vapor coming to the condensers is as nearly as possible at 850° C.

MR. W. F. BLEECKER: Can the furnace be used for the treatment of zinc-lead, sulphide ores, and if so, what provision is made for keeping the gases above from acting on the zinc? In the second place, in treating carbonaceous ores, what is to prevent the carbonic oxide from oxidizing the zinc even in the presence of the carbonaceous material?

PROF. RICHARDS: In treating carbonate ores, they are always calcined before being put into the zinc furnace, in order to remove the CO_2 which would otherwise interfere with the condensation. That is the practice in the retort process, and should be the practice in these furnaces. When smelting a zinc ore containing lead, the lead accumulates in the bottom of the furnace as lead bullion, and can be tapped out. If copper is present with enough sulphur to make matte, this accumulates in the hearth of the furnace, just as in a lead-smelting furnace.

MR. QUENEAU: How many kilos of zinc are reduced per kilowatt hour in the furnace? You were speaking of the

enormous capacity of the furnace, four or five times greater than in the usual lead furnace. Can you give us some figure as to the capacity of the furnace in terms of weight of zinc reduced and kilowatts furnished?

Prof. Richards: I have not in mind the actual pounds of zinc reduced and the current used. I figured up the efficiency from the data obtained as two tons of zinc per horse-power year. I know that compares very favorably with what is being done at Trollhättan in Sweden, where, I believe, they consume between three-quarters and one horse-power year per ton of zinc produced. This 25-kw. furnace, which I have seen in operation, is, I believe, working more economically of power than the large DeLaval commercial furnaces.

Mr. Bleecker (*Communicated*): A statement as to cost per ton of spelter produced by this furnace from a definite grade of ore would be interesting, because this will be the sole determining factor of successful operation. Unless the designer of this furnace can keep separate the sulphur and other gases and the zinc vapor, it is not clear why the greater proportion of the product should not be blue powder. These gases are surely present, because lead-zinc products containing sulphur cannot be roasted sweet.

Prof. Richards (*Communicated*): The variations in cost of ore, labor, power and fuel are so great, in different localities, that an estimate of detailed expenses of running would be of very little use. From the statements made in the paper that over 75 percent of the zinc in the charge is obtained in metallic form, that the small 25-kw. furnace worked at the rate of 2 tons per horse-power year, and that it is expected that a 500-kw. furnace would produce at the rate of 4 tons per kilowatt-year, it can be estimated, for any given locality, what prospects of commercial success are before Mr. Johnson's furnace.

A paper presented at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 6, 1911, President Wm. H. Walker in the Chair.

THE CONDENSATION OF ZINC VAPOR FROM ELECTRIC FURNACES.

By F. T. Snyder.

The development of every technical industry is characterized by change from a qualitative basis, in which progress depends on experiment and the trade skill of individuals, to a quantitative basis, in which progress is made by calculations from accurately obtained data. On the first basis, progress is slow and costly. The number of independent variables in each technical problem is large, and the choice of improper proportions for some of them often disguises the true effect of a change in the particular one under observation. On the quantitative basis, which may be called the engineering basis, progress is rapid and financially efficient, as the proper proportions of each group of variables may be mathematically equated between the groups, and the waste of time and capital in false construction avoided.

The condensation of zinc in the standard retort smelters is an illustration of the first condition—the basis of trade skill. The limiting technical factor in retort smelting is not the condenser, but the material of the retorts. This fact has shielded the design of the condenser from the commercial pressure for progress, the pressure for improvement in retort smelting being now on the retort. In its white-hot operating condition, the comparatively small mechanical strength of the retort material limits the load of ore a retort can carry to a few pounds. The melting point of this material is only a few degrees above the temperature required for smelting zinc ore. This puts a low limit to the rate at which heat can be forced through the walls of the retort. As only a small amount of heat arrives inside the retort per hour, only a small amount of ore is smelted and only a small amount of zinc vapor released to be condensed by the condenser. Through many years of experience, retort condensers have been propor-

tioned, on the basis of experiment and trade skill, to handle this slowly arriving volume of zinc gas with high efficiency. A fairly-well operated retort condenser will condense from the gas delivered to it something more than 99 percent of the zinc which is condensible under the temperature conditions at which the condenser is run. If a gradual increase could be made in the mechanical strength of retort material, the size of the retorts would be gradually enlarged, and it is probable that by a process of "cut and try," the proportions of condensers would keep pace with the demand for increased capacity up to, possibly, double their present capacity. The discovery of a retort material of very much better heat conductivity than the present clays would not materially increase the rate at which zinc gas could be delivered to a condenser, as the limiting factor in this direction is the low heat conductivity of the ore itself. To make heat flow faster into zinc ore than it does in retort smelting means that the outside of the ore must be heated hotter. If we heat it much hotter than in standard retort practice, the ore will begin to melt. If a retort material should be discovered that combined high heat conductivity with high mechanical strength when white hot, we could change the shape of the retort, and by spreading the ore out in a thin layer reduce the average distance the heat had to travel through the ore and at the same time increase the relative area of the heating surface. This would enable us to smelt more ore in a retort in a given time with the present temperature range and so deliver zinc vapor faster to the retort condenser. If this improvement in retort material should be very great, so that many times the present flow of zinc vapor could be delivered to a single condenser, the pressure of progress would be diverted from the design of the retort to the design of the condenser. If, in addition, the discovery of this hypothetical retort material of high capacity should come about suddenly, it is apparent that the trade-skill basis of progress in design would break down and there would be the necessity for engineering in the design of zinc condensers. This has been shown in the several cases where zinc retort furnaces have been built in which fifty to seventy-five retorts of standard size have been arranged to deliver their zinc vapor to a single common condenser. On checking the dimensions of some of these con-

densers on an engineering basis, it immediately develops that the proportions, as determined from trade-skill basis, are such as to make their commercial operation hopeless.

The electric smelting of zinc ore has produced a technical condition very much like that which would result from the discovery of such an improved retort material. With electric smelting of zinc ore the retort is eliminated, and with it disappear those limitations of size and temperatures which are inherent in the retort. The ore can be melted; can be heated, subject to certain commercial limitations, up to a temperature that will drive the necessary heat into the ore at a very rapid rate. It is now practical and convenient with electric smelting to deliver zinc vapor to a condenser at a rate three hundred to four hundred times the rate at which such gas reaches the standard retort condenser. It is at once evident that the trade-skill basis of design is inadequate and that the opportunity exists for the application of engineering methods to the design of zinc condensers. The metallurgical advantages of electric zinc smelting, outside of the question of condensation, are such as to bring a large and growing commercial pressure toward activity in this direction. The desirability of directing this activity in a fruitful direction will justify us in considering some of the engineering that may be applied to the design of zinc condensers.

General Statement of the Problem.

There are two standard engineering methods that may be applied to any problem. One is to work out with as great scientific accuracy as we may the detailed steps of a process and then follow it through mathematically. The other is to adopt a set of data which we know is operating satisfactorily under its conditions and, with the use, either consciously or unknowingly, of broad generalizations such as the conservation of energy or the persistence of motions, to transform this data to the conditions of the problem to be solved. We may with profit consider this condensation of zinc by both methods, taking up the latter method at this time and reserving the former method for a subsequent occasion.

The dimensions of the standard retort condenser and the conditions surrounding its use supply us with a set of reliable data

for our immediate purpose. As the dimensions of condensers and the practice of condensation vary somewhat from plant to plant, it will be clearer if we adopt a typical average condenser and average practice as to temperatures and rate of smelting. Figure 1 gives the dimensions of such typical condenser and its retort. The dimensions are given in centimeters. Cross sections are circular. The top of the condenser is hotter than the bottom. As this difference is small compared with the average temperature, we shall be within an allowable variation if we use the average of the top and bottom temperatures. The temperature of the gas delivered to the condenser varies considerably from hour to hour, but we shall be on the safe side in adopting the average temperature, as the condenser actually handles the maximum heat flow. The temperature of the condenser also varies

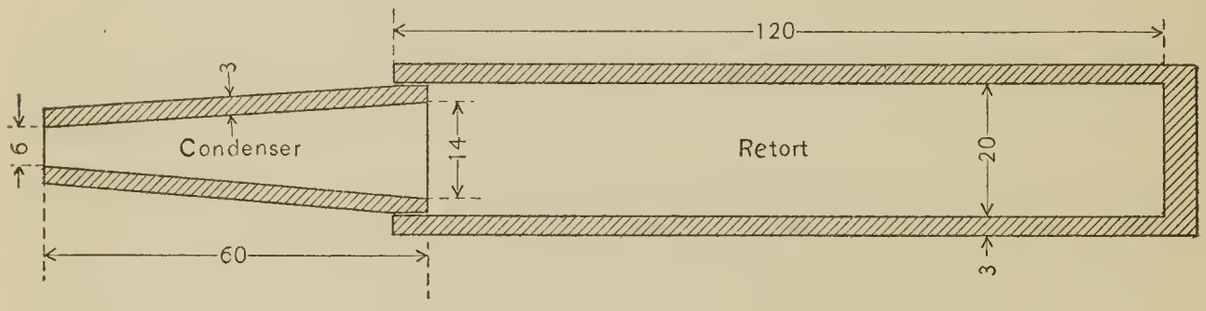

Fig. 1.

with the row the retort is on, but the average for a furnace will be on the safe side for capacity data. While the rate of flow of the zinc gas also varies from hour to hour, the same factor of safety for the average exists, as the condensers successfully handle the maximum rate of flow.

In this connection it may be pointed out that it has been commonly thought, on account of the difficulties met in trying to design large condensers on the trade-skill basis, that for some unknown reason it was more difficult to design a continuously operating condenser than one to operate intermittently. A little consideration will make it evident that it should be easier to design a condenser for a relatively stable set of operating conditions, than for varying conditions. As the condenser, to be commercial, must in any event handle the maximum flow of gas and the maximum input of heat, it follows that the condenser can be smaller for a regular flow than for any varying flow

delivering the same weight of zinc per day. One trouble with all the large condensers designed on the trade-skill basis has been that they have had only a small fraction of the condensing capacity they should have had. The electric smelting of zinc delivers a flow of gas that is quite regular in volume and temperature throughout twenty-four hours. If the flow had been irregular, for the same daily capacity, these undersized condensers would have been less able to handle the periods of maximum flow than they were the regular flow.

If, further, in arriving at our factors for engineering design, we adopt the condition that all the gases which are not involved in the reduction of zinc oxide (the water vapor, the carbon dioxides, sulphur dioxide and hydrocarbons from the reducing material), are driven off during the heating up period, before the condensation of zinc begins, we shall be on the safe side with regard to area of cooling surface and also with regard to the volume available for diffusion.

Detailed Consideration of the Problem.

The average temperature at which the mixture of zinc and carbon monoxide gases leaves the retort and enters the condenser will be taken as 1050°, and the average temperature at which the uncondensed gases leave the nose of the condenser as 600°. These are the temperatures along the axis of the condenser. In order to condense zinc and deliver it as liquid, the temperature of the inner surface of the condenser at the end next to the retort must be below the liquefying temperature of zinc vapor under the pressure conditions existing, and the inner surface of the small or nose-end of the condenser must be above the melting temperature. The melting temperature is 420°, and we can take the inside surface temperature of the condenser at the nose end at 450°. The boiling temperature of zinc at standard atmospheric pressure is 930°. To get at its liquefying temperature at the retort end of the condenser we shall have to consider the pressure conditions, as the boiling temperature varies with the pressure. Figure 2 gives the curves of the variation of the boiling temperature with changes of pressure as determined by Barus (U. S. Geological Survey, Bulletin 102, 1893). These curves have the advantage of having been determined experi-

mentally directly from zinc vapor and so do not depend on the constancy of Boyle's law, as do the curves that are obtained by transposition under Groshan's law (Pogg. Ann. LXXVIII, p. 112, 1849) from the vapor pressure curves of mercury. The mixture of gases, as delivered by the retort to the condenser, is substantially under atmospheric pressure. The flow of gas through the condenser is slow, so that the drop in pressure required to produce this flow is too small to be considered in connection with our immediate purpose.

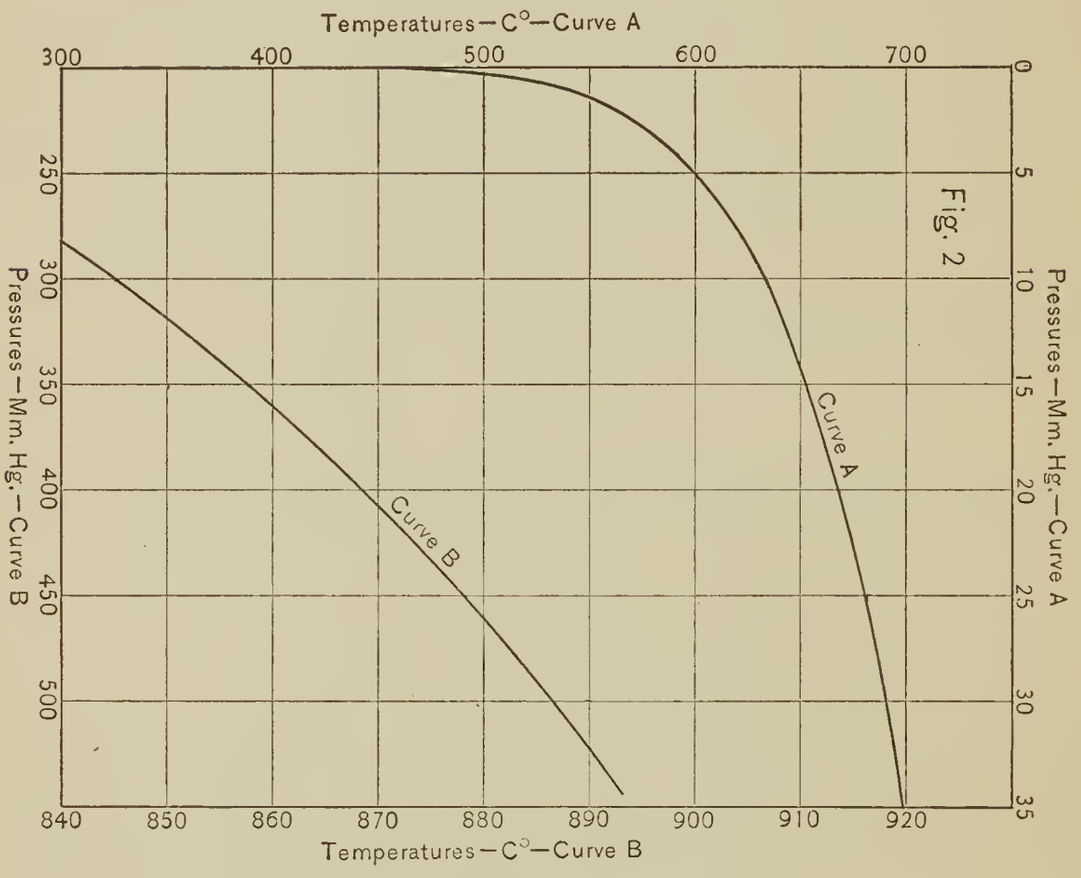

FIG. 2. Vapor pressure of zinc. (Barus).

Before we can determine what proportion of the atmospheric pressure is carried by the zinc, it will be necessary to determine the proportion of zinc in the mixture. For this purpose we can take the average charge of roasted ore to a retort as 20 kilograms carrying 60 percent or 12 kg. of zinc. With residues amounting to 50 percent of the weight of the ore in the charge, and analyzing 7 percent, the unreduced zinc left in the charge amounts to 0.7 kg. The vaporized zinc amounts to 11.3 kg. The corresponding amount of carbon monoxide produced by the reduction is 4.9 kg. Of the zinc reduced, 0.1 kg. on the average is lost

through the retort by leakage and breakages, and 0.4 kg. is absorbed by the material of the retort, leaving 10.8 kg. which is delivered to the condenser. As the relative volumes of each gas are inversely proportionate to their molecular weights, the zinc will carry 48.8 percent of the atmospheric pressure or 372 mm. At this pressure, by the Barus curve, zinc boils at 863°. We will take the average temperature of the retort end of the inner surface of the condenser as 850°, corresponding to the average temperature of 450° for the inner surface at the nose end. It is to be noted that these are the average temperatures of the surface of the condenser itself, and not the temperatures of the gas near the surface. The average temperature of the whole inner surface of the condenser will be the sum of the products of the circumference and temperature at each end, divided by the sum of the circumferences, as the condenser is conical. In calculating this average temperature we use the inner diameter, 6 cm. at the nose end, as shown in Fig. 1. For the diameter at the retort end of the condenser a correction is needed. The condenser is inserted into the retort 5 cm., so that the effective cooling length is 55 cm. with a total length of 60 cm. The corresponding diameter at 55 cm. from the nose end is 13.2 cm. Calculated with this diameter, the average temperature of the whole inner surface of the condenser is 725°.

As the liquid zinc is in the bottom of the condenser, which is cooler than the average of the top and bottom, the average temperature of the liquid zinc may be taken as 650°. At the temperature at which the uncondensed gases escape from the nose of the condenser, 600°, the vapor pressure of zinc is 5.0 mm. by the Barus curve. At this pressure and temperature 0.7 percent of the zinc which entered the condenser leaves the nose in the form of vapor. In addition to this vapor, zinc also leaves the nose of the condenser in the form of fume, but this fume has already given up its heat of vaporization to the condenser. There was delivered to the condenser 10.8 kg. of zinc. Of this about 0.1 kg. leaves uncondensed and the remaining 10.7 kg. is condensed by the inner surface of the condenser. With an effective length of 55 cm., a diameter at the nose of 6 cm. and an effective diameter of 13.2 cm. at the retort end, the condenser has an effective inner surface of 1660 sq. cm. The

space taken up on the sides by the plug in the nose is about made up by the area of the plug. We may take the distillation as active for 16 hours. There is therefore condensed by the condenser 10.7 kg. of zinc in 16 hours with an active cooling surface of 1,660 sq. cm., or an average rate of 0.40 grams of zinc per sq. cm. per hour. This is one of the factors we need for the engineering design of condensers. It is to be noted that it applies only to clay, with about the kind of surface used in retort condensers. The real cooling surface takes in the area of all the projections and indentations. To use this factor for other materials it will be necessary to introduce a co-efficient of roughness and determine it experimentally for each new material.

The 10.7 kg. of zinc which is condensed enters the condenser at 1050° and is cooled down to liquid zinc at 650°. In doing this it gives up 460 Calories per kg., or 4,930 Calories for the 10.7 kg. The carbon monoxide enters the condenser at 1050° and leaves it at 600°. In doing this it gives up 124 Calories per kg., or 604 Calories for the 4.87 kg. which accompanies the zinc. Together the gases give up 5,534 Calories in 16 hours, or 346 Calories per hour. This is absorbed by the 1,660 sq. cm. of the condenser surface at the rate of 0.21 Calories per sq. cm. per hour. This is the second factor we need for the engineering design of condensers.

As the mixture of zinc and carbon monoxide gas moves from the retort into the condenser, the outer layer next to the surface of the condenser begins to lose its zinc by condensation, and the zinc in the mixture away from the surface begins to move toward the surface by diffusion. As the mixture moves through the condenser, all the zinc which is condensed moves sideways an average distance of ⅓ the radius of the condenser. As the diffusion goes on at a determined rate, the speed of the mixture through the condenser must be such that diffusion will have time to move the zinc up to the cooling surface, while the mixture moves through the condenser.

At the temperature of 1050°, at which the mixture enters the condenser, both the 10.8 kg. of zinc and the 4.87 kg. of carbon monoxide gas occupy a volume of 36.8 cu. meters. They both occupy the same volume, each being diffused in the other. This volume of 36.8 cu. m. passes into the condenser in 16 hours, which

is at the rate of 2.29 cu. m. per hour, or 637 cu. cm. per second. The diameter of the condenser at the effective entrance at the retort end is 13.2 cm. and the cross sectional area 136.8 sq. cm., so that the average velocity of the gases entering the condenser is 4.67 cm. per second. At the temperature of 600°, at which the gases leave the nose of the condenser, the 4.87 kg. of carbon monoxide and the 0.075 kg. of zinc that leaves as vapor, each occupy a volume of 12.4 cu. meters. As this goes through in 16 hours, the rate is 0.78 cu. m. per hour, or 217 cu. cm. per second. The diameter at the nose end is 6 cm. and the cross sectional area 28.3 sq. cm., so that the average velocity of the gases at the nose end of the condenser is 7.67 cm. per second. The mean velocity through the condenser, which is obtained by dividing the mean of the volumes passing each end by the cross section area at the center, is 5.17 cm. per second. It is interesting to note that this mean velocity corresponds to an average time of 10.6 seconds for the passage of each part of the gas through the condenser.

At the retort end of the condenser, where the gases enter with an average velocity of 4.67 cm. per second, the distance through which the zinc has to diffuse on the average (⅓ the radius) is 2.2 cm., and at the nose end it is 1.0 cm., where the gases leave with an average velocity of 7.67 cm. per second. As the total pressure on the mixture of gases is constant, the speed of diffusion varies with the square root of the absolute temperature, and it will be convenient to introduce this as a co-efficient affecting the mean distance of diffusion, adopting as unity the speed of diffusion at 864°, the condensing temperature of the normal mixture of equal volumes of zinc and carbon monoxide. At the retort end of the condenser we have taken the temperature at the center as 1050° and at the surface of the condenser as 850°. The mean of these is 950°, and the temperature diffusion co-efficient, calculated from the square root of the absolute temperatures and referred to the rate of diffusion at 864°, is 0.96. At the nose end of the condenser the temperature at the center we have taken as 600° and at the cooling surface as 450°. The mean of these is 525° and the corresponding temperature diffusion co-efficient is 1.19. If we multiply the mean distance of diffusion at each end by its co-efficient, we will get the

equivalent distance through which the zinc would diffuse in the same time if the temperature were the standard, 864°. These are 2.11 cm. for the retort end and 1.19 cm. for the nose end.

The satisfactory operation of the retort condenser shows that with the velocity at which the gases travel through the condenser, the rate of diffusion is sufficiently rapid to move the zinc through the average diffusion distance in the time available. The relative velocity of diffusion sideways is proportional to the equivalent diffusion distance, and the ratio of this sideways diffusion velocity to the longitudinal velocity through the condenser is the third or diffusion factor that we need in the engineering design of large condensers. This ratio equals the product of the equivalent diffusion distance and the longitudinal velocity. For the retort end of the condenser, where the equivalent diffusion distance is 2.11 cm. and the average longitudinal velocity 4.67 cm. per second, the factor is 9.9, and for the nose end, where the equivalent half-radius is 1.19 cm. and the average longitudinal velocity is 7.67 cm. per second, the factor is 9.1. The mean factor for the whole condenser is the arithmetic mean of the factors at the two ends, and is 9.5.

We have now the reliable data from the standard retort condenser in convenient form for use in the engineering design of large zinc condensers. Collecting the factors in one expression, the result is that if we provide 1 sq. cm. of clay cooling surface (or an equivalent amount of some other material) for each 0.40 gr. of zinc to be condensed per hour, and if we arrange the thickness of the material of this surface and the temperature conditions at the other or non-condensing side of the material so that 0.21 kg. Calories of heat will flow through each sq. cm. of the surface per hour when the average temperature of the condensing surface is 725°, and if we arrange the volume inside the condenser, so that the product of the average longitudinal velocity of the gases in cm. per second and the average diffusion distance (corrected to the standard temperature of 864°) in cm., through which the zinc has to diffuse, is 9.5, then, the design of the large condenser will be on the same basis as the proportions of the standard retort condenser. It is to be kept in mind that only the cooling surface in the condenser that is between 850° and 450° counts in the production of liquid zinc.

As this upper limit of 850° depends on the atmospheric pressure, the reduction of the atmospheric pressure with high altitude is to be taken into account for a condenser so located. It is interesting to note in the standard retort condenser, the proportions of which have been determined by many years of "cut and try," that these proportions now in general use give a diffusion factor that is substantially constant throughout the length of the condenser. This means that these proportions represent the maximum commercial economy in the use of the condenser material.

So far in considering the matter we have taken the condensation as all occurring at the surface of the condenser. In practice a certain amount of zinc as fume escapes from the nose of the condenser along with the zinc that is in the form of uncondensed vapor. As the temperature, 600°, is well above the melting point of zinc, this fume is in the form of tiny drops of liquid zinc, which has condensed in the gas away from the surface of the condenser. Drops as small as these fall slowly. Clouds in the sky are made up of very small drops, and they fall so slowly as to appear stationary to casual observation. But these small drops fall with regularity at a constant velocity which can be calculated. The important point for us to notice is that the velocity of fall is constant and not rapidly increasing with time, as it does when a large heavy body falls through the air. If we consider a drop that starts to fall from close to the top of the condenser, it will move forward and downward on a diagonal line, the resultant of its constant velocity of fall and the velocity of the longitudinal movement of the gases through the condenser. To be saved, a drop which starts from a point near the top must do so at a distance sufficiently far back from the nose of the condenser to have time to fall to the bottom before the longitudinally moving gases reach the nose end of the condenser. All the drops that start from the top at points nearer the nose than this point will not have time to complete their fall and will be swept out of the nose with the uncondensed gases. There is therefore a wedge-shaped volume, lying with its base against the outlet end of the condenser, and tapering back along the top of the condenser, from which volume all the drops will be lost, by going out as fume with the uncondensed gases. The cubical contents of this wedge in different condensers

will be proportional to the product of the longitudinal velocity and the vertical distance of fall. The vertical distances bear the same ratio to each other in different condensers as do the ⅓ radii (or diffusion distances), so that between different condensers the volume of this wedge is proportional to the product of the longitudinal velocity of the gas travel and the diffusion distance. But this is the same factor that we have previously determined from consideration of the conditions of diffusion, so that if we properly design our large condenser to have the same proportions for diffusion that the standard retort condenser has, we will be designing it also to have the same proportions as to the amount of fume lost in the uncondensed gas.

An examination of the drawings of many zinc condensers that have been built or proposed for large capacity shows some means of applying heat to the condenser either internally or externally, by fuel fires, gas flames, or in most modern cases by electricity. As its name implies, a condenser is an apparatus for withdrawing heat, and it is evidently a contradiction of effort to also apply heat in any way. As the designers of these condensers understood this fact more or less, the probable purpose of this application of heat was to get the condenser up to the proper working temperature at the beginning of operations, or with a view of regulating it in operation to keep the temperature of the condensing surface within the right range. Consideration of the point shows that for both reasons it is unnecessary. If we design our condensing surface of such thickness of material and arrange the heat conditions at the non-condensing side so as to have the condensing side at 725° when the proper flow of heat per sq. cm. is passing through, then the surface will automatically keep itself at 725°. For if in any way we could get it hotter than 725°, this would increase the heat gradient to the other side and increase the rate of flow through the surface above the rate at which heat was being received from the condensing zinc and as the surface would be losing heat through its material faster than it was receiving it, the surface would cool down to the 725° for which it was designed. The reverse action would take place if we could in any way cool the surface below the temperature for which it was designed. The change in the heat gradient would soon bring it up to the designed temperature. In starting up

a new and cold condenser, it will only be a short time before the heat from the zinc brings the temperature of the condensing surface up to the temperature for which it is designed. There is no practical need for extra means of heating.

It will be interesting in the light of the data that we have secured to examine the design of one of the large condensers which have been built. Such a condenser is described in connection with the Lynen furnace. (Ingalls, Metallurgy of Zinc, p. 486.) This condenser is a rectangular chamber of brick, 1.2 meters high, 0.36 meters wide and 3.4 meters long. This chamber is divided into three compartments by vertical, longitudinal fireclay partitions. The gases are discharged into the two outer compartments by the retorts, 36 retorts to each outer compartment. The gases move vertically upward in the outer compartments, and uniting at the top move downward in the center compartment to the carbon monoxide outlet. Running longitudinally through the compartments are a number of horizontal iron pipes 6 cm. in outside diameter. The condenser was cooled by blowing air through these pipes. The outer walls of the chamber and the bath of zinc forming the bottom of the chamber were so designed as to be able to absorb no practically important amount of heat, so that the entire condensing was done by the air pipes.

There were 19 of the condensing tubes, 6 cm. diameter and 340 cm. long, making a total condensing surface of 122,000 sq. cm. In normal operation the 72 retorts using this condenser would deliver to it 48.2 kg. of zinc per hour, which is at the rate of 0.40 gr. per sq. cm. per hour. This is the rate we found in use with the standard retort condenser. This Lynen condenser therefore had ample cooling surface. Divided over this cooling surface, the flow of heat provided by the zinc in cooling down and condensing amounts to 0.21 Calories per sq. cm. per hour. For the condenser to work successfully we have seen that the air cooling must be such that with this rate of heat flow the condensing surface will keep about 725° on the average and that the cold end will not be below 450° and the hot end not above 850°. This is on the condensing side of the pipes. It will take about 1° drop in temperature to get heat to flow through the iron of the pipe at this rate of 0.21 Calories per sq. cm. per hour, and it

will take a drop of about 179° to transfer this heat from the inner surface of the pipe to the air in the time available as the air rushes along. The temperature of the air as it enters the pipes at the cool end will therefore be 450°, less the sum of 1° and 179°, or 270°, and as it leaves the hot ends will be 850° less the sum of 1° and 179°, or 670°. To absorb all the heat given up by the zinc of the 72 retorts and do the absorbing between these temperatures of 270° and 670° will require the passing of 72 cu. meters of air per hour as measured at atmospheric pressure and temperature. This corresponds to a velocity of about 150 cm. per second through the pipes for the warm air. This velocity is good economic practice. The pressure drop between the cool and hot ends of the pipes would have to be kept at the point which would keep up this rate of flow in the air. From the drawing it looks as though the convection flow of air was expected to do this, but convection would produce only a very small fraction of the air current required. If the air had been forced in at atmospheric temperature, 20°, only about ⅔ as much would have been required, but about ⅜ of the length of each tube would have been below the freezing point of zinc and so we would have zinc dust in place of liquid zinc. This would soon have clogged up the cooler end of the condensing chamber, whereas with the proper amount of air at the proper temperature all the surface of the tubes would be available for producing liquid zinc.

In this Lynen condenser the width of the condensing space was about 6 cm. and the average velocity of flow of the gases after entering the condenser 7.76 cm. per second, so that the product of the diffusion distance and the velocity was 23.3 as compared with the average of 9.5 which we found as the diffusion factor of the standard retort condenser. This condenser was therefore deficient in the time it provided for diffusion. From the factors we should expect that about one-half of the zinc would have time to diffuse over the condensing pipes, and the other half would be swept out of the condenser with the uncondensed gases. The condenser as it was proportioned had diffusing capacity enough to handle the zinc from 36 retorts, but with 72 retorts it only had diffusing capacity to stop about one-half of the zinc delivered to it.

DISCUSSION.

MR. C. A. HANSEN: We have collected some 1,200 pounds of zinc in the condenser of an electric furnace during one short run—only ¾ pound blue powder, by the way, as a by-product—and have sold it at the market price of the best zinc. I heartily agree with Mr. Snyder that the only weak spot in the electric zinc furnace is not in the furnace at all, but in the condenser. When it is realized, as I believe some do realize now, that a condenser must get rid of almost as much energy as is developed in the furnace itself, and that without exceeding a temperature of 650° C. or thereabouts at its inside surface, there will be less designing of 200-500 kw. furnaces with condensers that could not dissipate 20 kw. without getting red hot outside. As for the furnace, it is almost impossible to design one that won't distil zinc.

MR. F. L. CLERC (*Communicated*): I am inclined to think that Mr. Snyder overlooks the relative efficiency of suspended liquid globules in surface condensation. My own observations and experiments lead me to think that the growth of these globules is quite rapid.

MR. SNYDER (*Communicated*): Mr. Clerc speaks of the efficiency of the suspended zinc particles as condensation surfaces. Actually the efficiency is low. This is due to two reasons. First, such drops can only condense zinc on themselves as fast as they can radiate the heat of vaporization. This radiation rate is slow, as both the absolute temperature of the drops is comparatively low and the temperature range from the drops to the cooling surface is small. Second, as the excess vapor varies inversely with the radius of the drop, the re-evaporation from the small drops is rapid.

A paper read at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 8, 1911, President Wm. H. Walker in the Chair.

ELECTRICALLY FUSED ALUMINA—"ALUNDUM"—AS A REFRACTORY.

By L. E. Saunders.

In the earliest endeavor to preserve primitive fire, it became necessary for its users to have a container for it. It is therefore probable that the first experimental work ever undertaken on refractories was the search of our prehistoric ancestors for an earth or rock which best conserved and protected the feeble flame which they had not yet learned to produce.

The term "refractory" has, since then, taken on a wider and wider significance as the demands on refractory bodies have increased. The meaning now attached to the word varies almost with the user of it and the use to which the body is to be put.

There are some common properties, desirable in all refractories, however, such as high melting point, mechanical strength at high temperatures, low coefficient of expansion, and resistance to abrasive action. These are well recognized as refractory essentials, or, at least, desiderata, and I will not further discuss them at this time or more than mention now other properties, such as thermal and electrical conductivity, and resistance to chemical action, which are desirable or essential only in special cases. I would now only call attention to the fact that it is but rarely that the material selected fulfils all the requirements, and it is usual to choose a kind having the least of the ills that refractory materials are heirs to.

The substance I wish to bring to your attention to-day, as one having many of these desirable refractory properties, is electrically-fused alumina, bearing the trade name of "Alundum." It was primarily developed for abrasive purposes, but its heat-resisting properties were so often urged that it led to its introduction into this field.

There are two forms of Alundum of interest to us here—

first, a white crystalline product, having less than 1 percent of impurities; and, second, a reddish-brown vitreous material, having from 6 to 8 percent of impurities, these consisting in both cases of oxides of iron, titanium and silicon. They are both electric furnace products from the mineral bauxite, having undergone different degrees of purification. The purer white product has a melting point between 2050° and 2100° C.; the brown product not more than 50° lower. The coefficient of linear expansion for the white product is 0.0000078, and for the brown material, 0.0000085. The thermal conductivity is about twice that

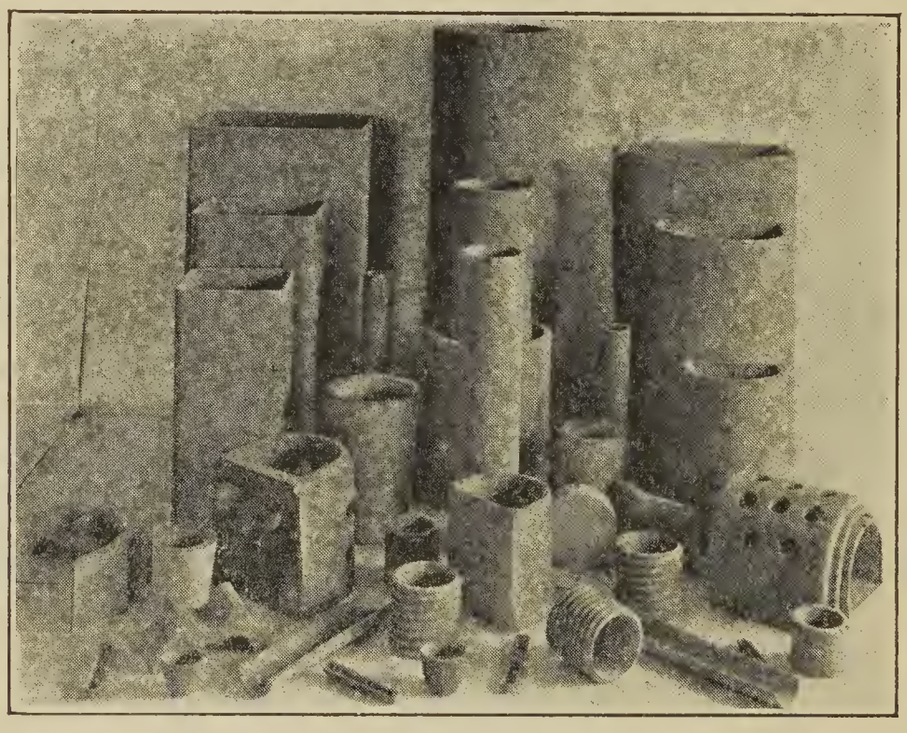

Fig. 1. General Display.

of Marquandt porcelain, and three to four times that of most fireclay. The hardness in Mohr's scale is above 9, but lower than 10. The specific gravity in both products varies between 3.93 and 4.00. Both kinds of product are quite unattacked by aqueous acids and alkalies, and very superficially by fused alkali carbonates. Basic or acid slags dissolve it with some difficulty, acid slags having a readier action.

Some attempts at moulding it from the liquid condition have met with partial success, although the difficulties involved are so great that only very simple and crude forms have been made.

The method of application which has been found easiest, and of which most of these specimens are examples, consists in mingling the crushed grains (the purer form is mostly used) with a binding agent of a refractory and ceramic nature, moulding the desired pieces after the manner of the potter, and burning them in a ceramic kiln. The resulting articles are more refractory than the binding agents employed, and, in nearly every case, than amorphous alumina. This is also true of the unbonded product, even in fine powders, and it is a fact for physical chemists to explain. The amount of bond is varied in different forms, but in none of these articles does the melting point drop below 1950° C. Other properties have changed but slightly.

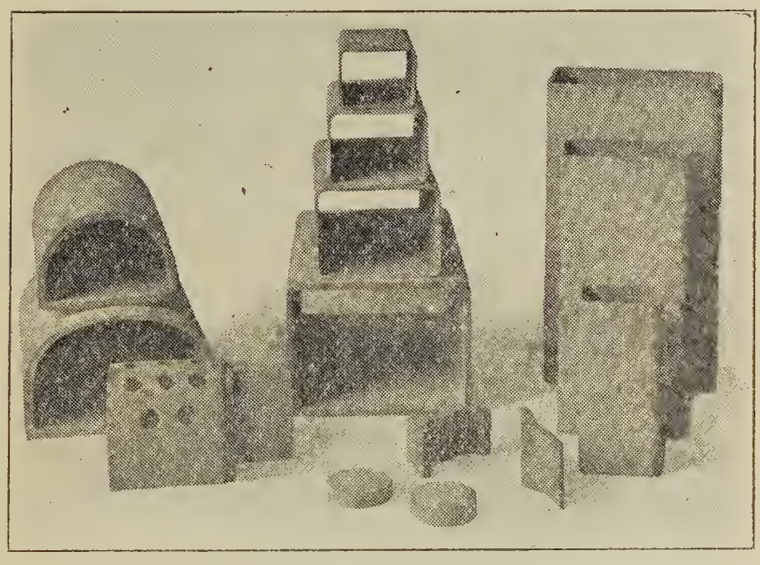

FIG. 2. Muffles of Various Shapes.

For instance, the linear expansion coefficient is, in the more refractory bonded bodies, 0.0000071. The thermal conductivity is still twice that of Marquandt porcelain. The strength, both tensile and compressive, is very high, even at high temperatures. The electrical resistivity, as determined by Dr. M. deKay Thompson, is as follows:

At	535° C.—	47,600,000	Ohms per cm. cube.
At	721° C.—	4,900,000	" " " "
At	908° C.—	2,400,000	" " " "
At	1040° C.—	750,000	" " " "

The muffles shown here are distinguished by high thermal

conductivity and high melting point. They have four to five times the life of the ordinary clay muffle in gas furnace work. They are especially adapted to the electrically-heated wire-wound type of laboratory furnace. They have the advantage over quartz of being more refractory and of higher tensile strength. They are porous and cannot be used where entirely gas-tight furnaces are required.

The tubes are similar to the muffles, and have found chief

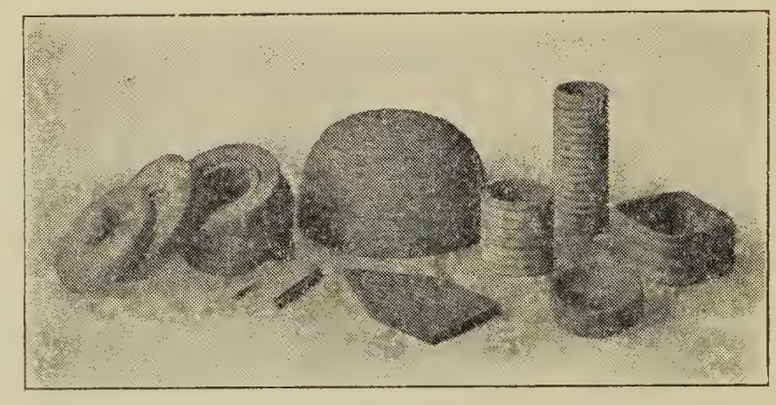

Fig. 3. Electric Furnace Tubes.

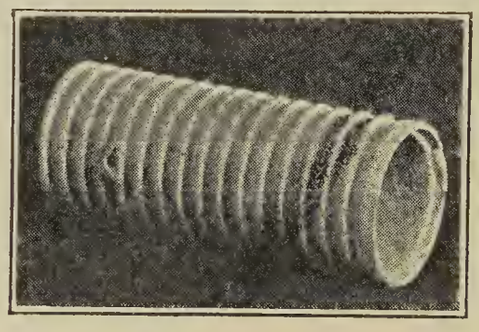

Fig. 4. Electric Furnace Core.

use along the same lines. They are also porous, and cannot be used for pyrometer protection tubes.

The crucibles are made of varying density, but are still porous in all cases. This prevents their use in fusing slags or salts, but metals, even platinum, may be melted without injury to the crucible. This seeming disadvantage of excessive porosity has been turned to good account in the laboratory sizes. They answer all the purposes of a Gooch filtering crucible without the trouble of preparing the asbestos blanket, and the porosity can be so controlled that the most finely divided substances may be cleanly filtered. The usual analytical precipitates are quickly and surely

separated, and may be ignited quickly in the crucible on account of its high heat conductivity. Even deflocculated graphite may be separated from its suspending medium.

Large filtering dishes are also made, and have been found useful in making organic preparations and in bacteriological work. An extraction thimble for the Soxhlet or similar apparatus is very useful, as it may be cleaned simply by ignition over a burner and used repeatedly.

Combustion boats of various sizes are valuable on account of

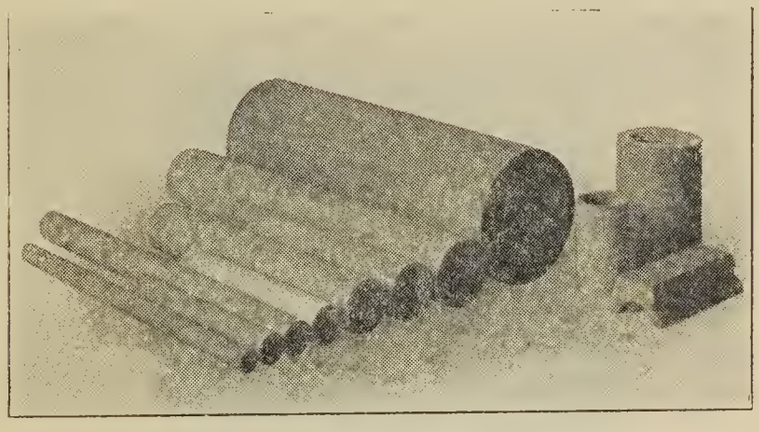

FIG. 5. Tubing.

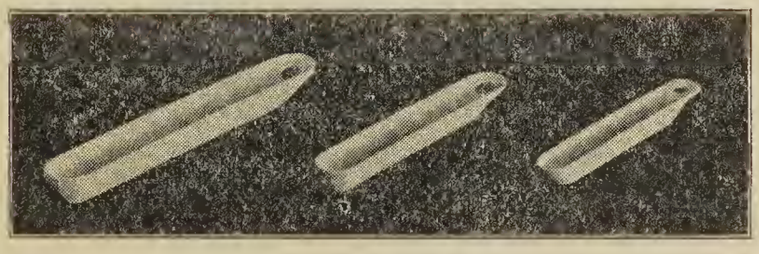

FIG. 6. Combustion Boats.

good heat conductivity, mechanical strength and chemical inactivity. If it is desired to use a boat of some other material, some carefully prepared alundum grain, free from carbon, sprinkled over the bottom prevents the sample from sticking in an oxygen combustion.

A useful modification is Alundum cement, which may be used to coat the inside of crucibles and furnaces for high temperature work. It does not melt or combine with carbon below 1950° C., and may be used for lining larger-sized crucibles than it has seemed practicable to make entirely of alundum.

Enough of these articles have been described to show that there is a wide field of application and that it is possible to produce almost any shape that may be desired. Indeed the greatest difficulty so far encountered is that each user desires a different shape or size, so that it has been impossible to prepare the usual stock.

It will be noticed that mostly all of the forms shown here are of laboratory or semi-commercial types. Little mention has been made of the larger commercial uses. By the very nature of the process of manufacture, such a substance is costly, and in excuse

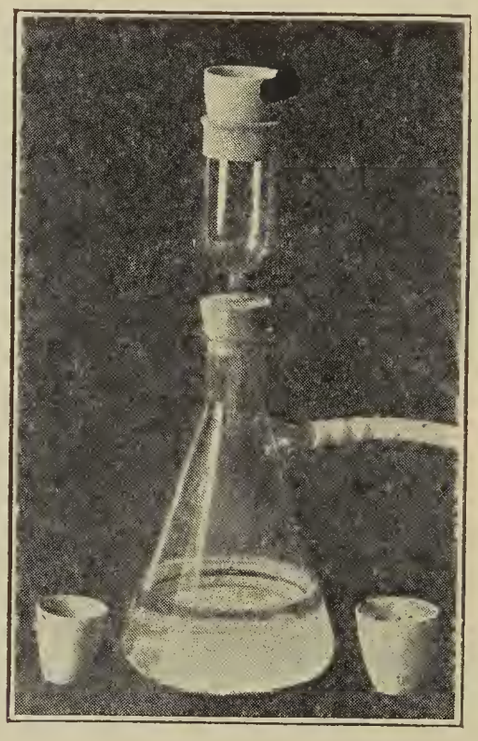

Fig. 7. Gooch Filter.

for the early development of the small articles, rather than more commercial forms, it may be said that the cost of the material entering into their composition is relatively small, while in the case of bricks it is relatively great.

Some work has been done, however, on testing out Alundum bricks. A Héroult furnace in the experimental department of our Niagara plant was equipped with a roof of these bricks in April, last year. Since that time the furnace has been used at intervals totaling about three months, actual running time, with some 40 or 50 shut-downs, and the roof is still in useable condi-

tion. It may be added that the temperatures used are decidedly higher than in the steel furnaces, so high, in fact, that a regulation silica roof previously tried went down in five to six hours.

A trial is now under way in the Héroult furnace of the Halcomb Steel Co., and at this writing the roof has outlasted two silica roofs and is still in fine condition, as reported in a telegram just received. Until this and other trials are complete, no claims will be made for Alundum brick. It may be said at the outset that they cannot economically be used in contact with slags, either acid or basic, nor can they be usefully employed where the present refractory life is very long. It is desirable to leave further reference to them for a later communication to the Society, should the completed data have a favorable aspect.

In this outline it is thought that enough has been said to indicate that this new product may be of assistance in the development of high temperature work.

DISCUSSION.

PRESIDENT W. H. WALKER: Ideas are like forces—they do no work until they are put in motion. To put ideas into practice we need tools, and Mr. Saunders has given us some good examples of new products available for our use.

PROF. S. A. TUCKER: What methods were used in determining the melting points?

MR. SAUNDERS: It was done by means of an optical pyrometer, and was checked by the Bureau of Standards, the two results being concordant.

MR. F. A. J. FITZGERALD: Could you give results on the comparative melting points of various refractories, such as silica, magnesia, etc.?

MR. SAUNDERS: I have done exactly that thing within the last week. I thought that question might be asked, and so I heated, under exactly the same conditions, samples of commercial, so-called refractory bricks. These were actual pieces of bricks

chipped off and shaped up into cones. The order of melting is as follows:

1. Silica.
2. Chrome.
3. Beauxite.
4. Brown Magnesite A.
5. Brown Magnesite B.
6. Grecian Magnesite.
7. Alundum.

Mr. F. A. Lidbury: Has Mr. Saunders any figures showing the solubility of the articles which are made for laboratory purposes in the ordinary laboratory reagents? How do they compare with materials which are ordinarily used for the same purpose? In regard to the statement in the paper that crystallized alumina has a higher melting point than amorphous alumina, a parallel case is to be found in the monoclinic and rhombic forms of sulphur, where the stable modification also has the higher melting point. In the present case you can either assume that the crystalline form of alumina is more stable than the amorphous form, or that the amorphous form is really undercooled liquid alumina with extremely high viscosity, in which case the melting point is the point at which the viscosity becomes small. In either case it is interesting to observe that it should be possible to melt amorphous alumina, and while maintaining the molten mass at a lower temperature than the melting point of the crystalline form, cause it to solidify by the addition of fragments of the crystals.

Mr. Saunders: In reply to the first question, I will say that some solutions, such as might be met with in analytical work, have been passed through these filtering crucibles in a much more severe manner than will ever be used in analytical work, with these results: The first treatment with almost all of the reagents, sulphuric and hydrochloric acids, potassium and sodium hydroxids, did take away a little weight, but in no case exceeding 0.03 percent. After the first treatment the loss was so very small that it was difficult to determine; it was in the thousandths of one percent. Apparently the first treatment washes out a little dust caught in the pores, and it is to be recommended that

anyone using them give them a preliminary washing before they are used for analytical purposes.

MR. CARL HERING: At what temperature does the material begin to soften? For practical purposes it is generally the softening temperature which would limit the use of the material.

MR. SAUNDERS: The solid alundum has an exceedingly sharp melting point; it does not soften, I should say, until within a hundred degrees of its melting point. It is quite firm and solid at 1950° C., and its bonded forms are strong enough for platinum to be melted in them. At this temperature, 1775° C., it is quite strong and uniform.

MR. HERING: But not at 1950°?

MR. SAUNDERS: They are strong enough to hold together at 1950°.

MR. HERING: If under pressure, at what temperature would they change their shape?

MR. SAUNDERS: At 1950° I should expect them to change shape under pressure.

MR. HANSEN: With reference to Mr. Saunders' use of an alumina roof in an electric steel furnace, I wish to say that some three years ago I requested quotations from the Norton Company for alumina brick, stating that I wished to use them as roof material in an electric steel furnace. The price quoted, some $900 per 1,000, discouraged the experiment. Ordinary silica brick which they would replace were worth $20 to $25. It is not necessarily true, however, if an alumina roof, at $700 for material and $10 for labor in assembling it, lasts only 15 or 20 times as long as a silica roof, costing $20 for material and $10 for labor, that the alumina roof is the more expensive. Nor is it at all true that the relatively short life of the silica roof is determined by the melting-point of silica, as is shown by the following facts:

Analyses made of stalactites knocked off from a silica roof of an electric steel furnace showed the following compositions:

	Normal brick	*Base of stalactite*	*Tips of stalactites*
SiO_2	95.17	92.16	76.33
CaO	2.53	2.79	9.74
MgO	0.03	0.49	7.94
$Fe_2O_3+Al_2O_3$	2.27	3.68	3.88

The basic material had been vaporized under adverse, yet very common, conditions of arcs and slags. Silica, of course, readily picks up basic fumes, and when the furnace is working such a roof will drip at any working temperature. When it does drip, it entails a lot of expense, properly chargeable to the roof. The acid slag formed scours the furnace banks, thus raising the maintenance cost, and the acidity may prevent the making of the proper composition of steel, which, when working under narrow specifications, might be condemned. This is particularly true when high carbon steels are required low in silicon. I have seen such tests go up nearly to 2 percent silicon, due to reduction of silica in the slag by carbon in the steel and by the electrode carbon. A highly silicious slag has so high a resistance that the electrodes must dip well into even a thin slag, furthering the reduction of silica by the electrode carbon. There are, of course, ways of guarding against some of these evils, but they all cause delays, often serious ones, and all add to the production cost charges which should be properly considered under the roof-cost item.

If an alumina roof will not pick up basic fumes, it should have a very long life, and in no case would the furnace difficulties incident to the use of a silica roof be encountered.

I have also made use of carbon roofs in electric steel furnaces, which are really admirable in many ways, but are useable only when electrodes at the same potential pass through the roof. They may be covered with sand to cut down heat losses, and they do not burn away as fast as one would suppose.

MR. J. W. BECKMAN: Has Mr. Saunders had any experience with alundum, heated continuously to about 600° C., in alternatingly a reducing and an oxidizing atmosphere? Some time ago I had occasion to work with several tons of alundum, granulated to about No. 16 grain, submitting it to the conditions mentioned, and after a month or two the material was no longer in grain form, but was the finest powder imaginable. I tried to explain this behavior of the material by its heat expansion, but I saw stated at the time, in an issue of the *Electrochemical and Metallurgical Industry,* that alundum as it is made by the Norton Company has even a smaller coefficient of expansion than glass or platinum. I therefore have come to the conclusion that this

breaking up of the material is due to a re-arrangement of the molecular structure of the alundum.

MR. SAUNDERS: I would like to say one word first in regard to Mr. Hansen's remarks. I think he was a little inconsistent. He objects to paying $900 per 1,000 for bricks, and yet he says that they are worth from 15 to 25 times as much as the silica roof.

A MEMBER: At what temperature does the combination of the alundum with silica or lime begin?

MR. SAUNDERS: I do not know the temperature; but it is pretty low—probably in the neighborhood of 1500° or 1600° C.

PROF. J. W. RICHARDS: I think that the high conductivity of this new material would make it an ideal material for zinc retorts, if it could be used for that purpose. Where heat has to be sent through a thick retort, if it has three or four times the conductivity of ordinary fire clay, it should be highly advantageous to use it for that purpose if it is not too porous, or if its injurious porosity can be overcome by a special treatment. I think we should consider, in using it for the roof of a steel furnace, the large loss of heat through the roof, caused by its great heat conductivity. This latter quality is so high that the heat losses through the roof may be abnormal, unless proper precautions are taken to cover the outside of the roof with a less conducting material.

MR. SAUNDERS: While the heat conductivity of alundum brick is not greater than that of silica brick, used almost exclusively in electric furnace roofs, it would be a simple matter to put another layer of bricks on top of them, if too much heat is lost by conduction.

In regard to the disintegration of alundum referred to by Mr. Beckman, it was undoubtedly due to the rather high coefficient of expansion of the material, and the heating and cooling to which is was subjected probably shattered the grains.

MR. QUENEAU: Will Mr. Saunders give us the numerical value of the heat conductivity?

MR. SAUNDERS: The comparative heat conductivity?

MR. QUENEAU: "Has twice the conductivity of porcelain" does not give us any very definite information; neither does "five or six times that of clay," because clay will vary five or six times according to the type of clay.

MR. SAUNDERS: Chemists are more familiar with porcelain than almost any other laboratory refractory, and that is the reason the figures were given in that way. We have no absolute figures.

MR. QUENEAU: How did you make the comparative determination?

MR. SAUNDERS: That would be rather a long story, to describe the apparatus and arrangements that were used to determine the temperature, and while there may be errors in the determinations, the errors were all alike; that is, on the different materials the same methods were used. We have no absolute figures.

DR. WHITNEY: Is the company prepared to sell tiles with holes drilled through them?

MR. SAUNDERS: They have been made.

A paper presented at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 8, 1911, President Wm. H. Walker in the Chair.

THE ADVANTAGES OF KEOKUK, IOWA, FOR ELECTRO-CHEMICAL INDUSTRIES.

By Frank P. H. Knight.

The Water Power Development.

One of the great engineering projects of the United States, of interest to the electrochemical industry, is the great power dam that is being built across the Mississippi River at the foot of the Des Moines Rapids at Keokuk, Iowa, by the Keokuk and Hamilton Water Power Company.

The river at this point is about three fourths of a mile (1.2 km.) wide and has a fall of about 23 feet (7 m.) in eight miles (13 km.). The bed of the river and the bluffs on each side are practically solid limestone, belonging, geologically speaking, to the Sub-carboniferous Age. Some of the strata of this formation are noted for the fine fossils and geodes that they contain.

Fig. 1. General View of Completed Dam and Power House.

The dam will be about seven-eighths of a mile (1.4 km.) long and 32 feet (10 m.) high, above the river's bed, giving an operating head of from 21 to 39 feet (6.5 to 12 m.), according to the stage of the river. It will be a concrete monolith.

The power-house will be below the dam, parallel with the river, on the Keokuk side. It will be 123 feet (37 m.) wide by 1400

feet (430 m.) long. The sub-structure is of massive concrete. Height, from foundations to roof, 133 feet (40 m.). There will be 30 units, consisting of two turbines below and a generator above, on the same shaft, of 4000 h. p. capacity.

The present government canal, about eight miles long (13 km.), with its three locks and dry-dock, will be entirely submerged, and a much larger lock and a new dry-dock will be built. The deep water and the time saved in lockage will be a great aid to navigation.

The initial installation will be 120,000 h. p., which it is expected will be completed in two and one-half years; this will be increased later to 200,000 h. p.

FIG. 2. Excavation for Dam on Illinois Side.

Commercial Advantages.

The exact rates to be charged for power locally have not as yet been announced. The company expects to get an average income of $20 per h. p.-year. It is to be delivered at St. Louis, about 170 miles (280 km.) south, at $25 per h. p.-year. As the company wants to sell as much as possible near the generating point, rates will be made in proportion to the distance from Keokuk, and to the amount used.

Natural Resources.

The river water is clear and pure enough for most manufacturing purposes during the greater part of the year. The greatest impurity at any time is suspended clay, which is readily removed by alum or ferrous sulphate and lime.

The different limestone strata of the locality vary in purity; some are quite pure, while others carry silica, alumina, or magnesia.

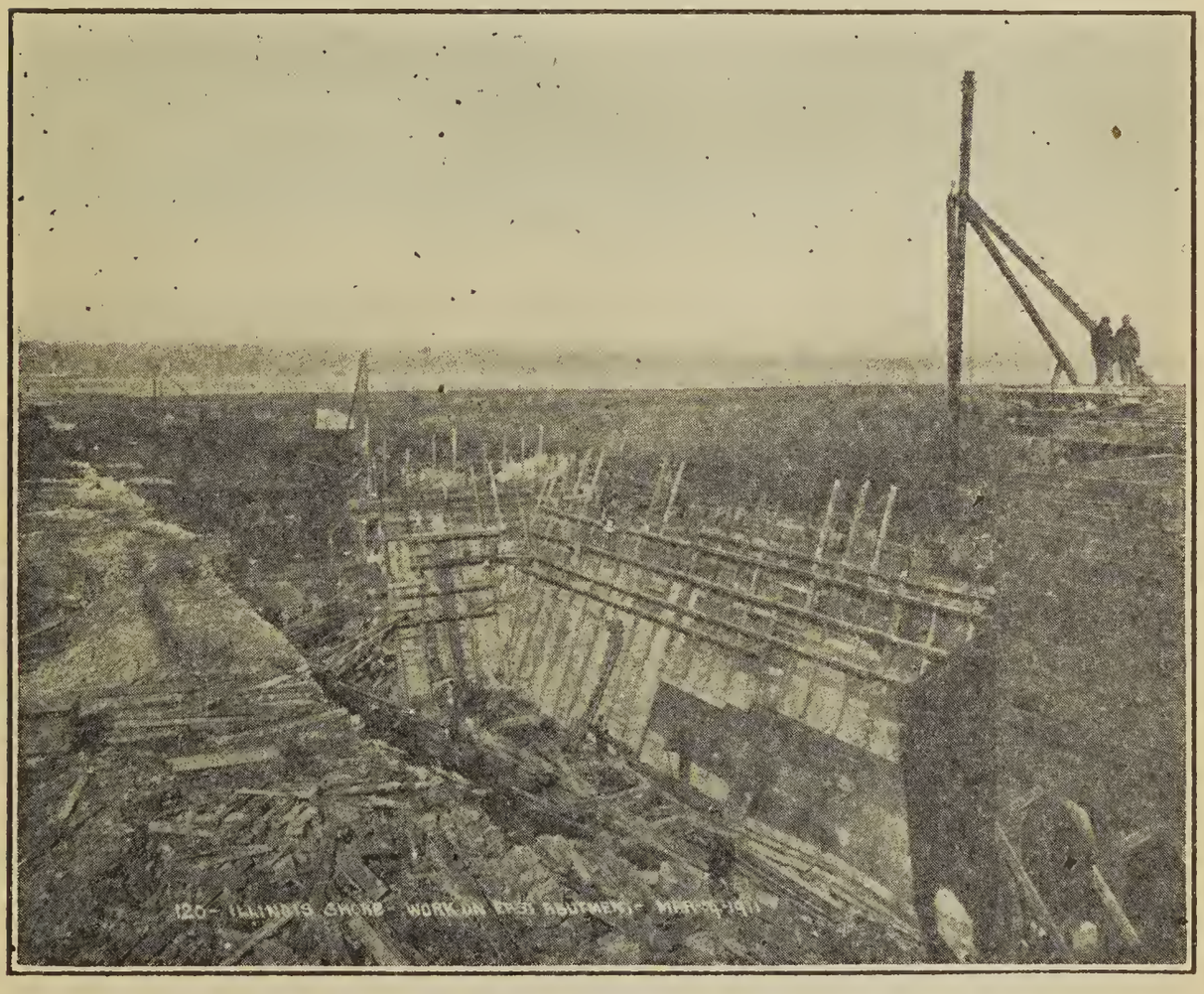

FIG. 3. Work on East Abutment, Illinois Shore, March 14, 1911.

Good sand of almost any degree of fineness suitable for the manufacture of carborundum or other silicon compounds can be obtained in almost unlimited quantities from the Mississippi or Des Moines Rivers.

The nearest producing coal mines are about 35 miles (58 km.) from the river, both in Iowa and Illinois.

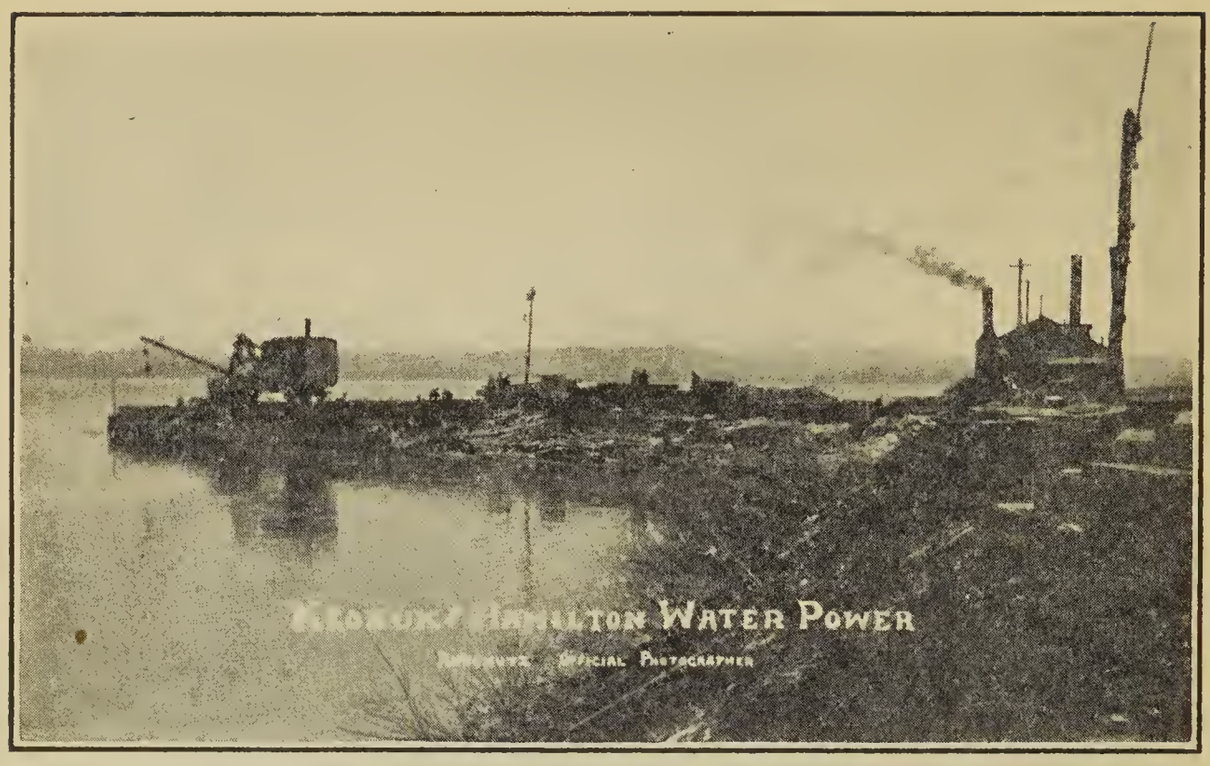

FIG. 4. Beginning of Coffer Dam on Iowa Shore. Up-stream Side.

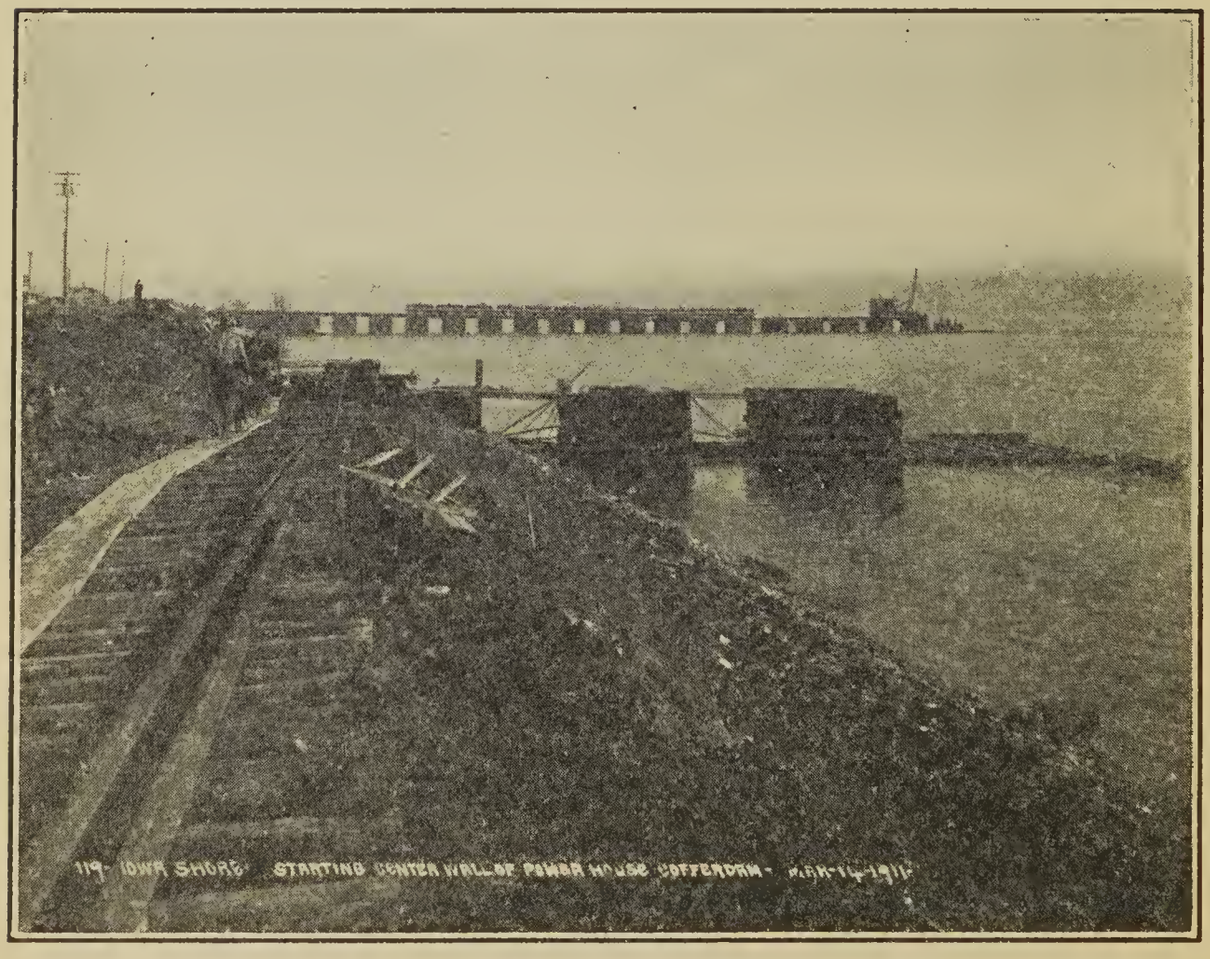

FIG. 5. Iowa Shore. Starting Center Wall of Power House Coffer Dam. March 14, 1911.

Transportation.

Keokuk has four railroad and two steamboat lines. The river is navigable from St. Paul to the Gulf of Mexico the greater part of the year, and river transportation is much cheaper than, and practically as quick as, by rail.

Factory Sites.

There is plenty of ground suitable for factory sites on both sides of the river above and below the dam, either on the bluffs or at the water's edge.

The main part of the city is located on the bluff, high above the river. It has a population of 15,000 and does a good manufacturing and wholesale business. It is the best jobbing point between St. Louis and St. Paul.

About a year ago the commission plan of city government was adopted which has proved to be very efficient, economical and generally satisfactory.

An industrial association has recently been organized and properly financed, which will do everything in its power to induce new industries to locate here.

The author has lived in this locality nearly thirty years, and is well acquainted with the flora, fauna and geology of the region, as well as the commercial enterprises hereabouts. He will be pleased to furnish anyone with any additional information that may be required.

A paper presented at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 8, 1911, President Wm. H. Walker in the Chair.

THE ADVANTAGES OF MAINE FOR ELECTRO-CHEMICAL INDUSTRIES.

By C. Vey Holman.
State Geologist of Maine.

The advantages which Maine offers for the development of electrochemical industries may be considered as geographical, meteorological and geological. I shall treat of them briefly in that order.

Let us consider first, then, the geographic advantages. Largest of all the New England States, in fact, falling short by only 1,200 square miles (3,600 sq. km.) of equaling within her borders the aggregate area of all the other five, the State's territorial expanse of 31,500 square miles (87,500 sq. km.) lies as nearly as possible midway between the Equator and the North Pole, the 45th parallel of north latitude practically bisecting the State. Projecting to the eastward far beyond the general Atlantic coast line of her sister States, with a seacoast which, measured in a direct east and west line, spans only a little more than 200 miles (325 km.), but the sinuosities of which are such as to afford nearly 3,000 miles (5,000 km.) of deep, bold shore front on the Gulf of Maine, the State is distinctly maritime. This continental position places Maine in the direct draft of the humid southwest winds from the Gulf of Mexico, the return trades of the north temperate zone, while ensuring the laving of her coasts by a constant circulation of frigid waters discharged from the Arctic Ocean, through the channels bounded by the east coast of Labrador and the west coast of Greenland, into the Gulf of St. Lawrence and thence down along our north Atlantic seaboard, impinging at a distance of some marine leagues upon the northward-flowing thermal waters of the Gulf Stream.

Enjoying thus substantially equal ocean exposures on both the south and east, Maine is favored with winds from practically

two-thirds of the points of the compass blowing directly from the ocean or charged with oceanic influences which render them moist and cool.

All these circumstances, it will be observed, favor periodic—that is to say, regular and constant, rather than non-periodic and fluctuating—precipitation of moisture over the entire geographic area of the State. They also tend to check evaporation and favor storage conservation of stream flow. The winds are variable, shifting with frequency to all points of the compass, and therefore bear in rapid alternation a varied succession of dampness and dryness, of cold and heat, ensuring against excessive drought on the one hand and freshet floodings on the other. The mean annual precipitation ranges from 35.3 inches to 52 inches (90 to 130 cm.), the rainfall being distributed with remarkable uniformity throughout the year, a fair proportion of it occurring in each of the four seasons. The summers, though short, are climatically delightful, beginning with comparative suddenness in June and ending with abruptness in September, to be followed by a bracing autumnal season, of which the languorous Indian summer forms the charming prelude and the period of exhilarating sunny days and clear, frost-laden nights following the harvest moon constitutes the health-giving close. The winters are long, beginning frequently in November, reaching their height in mid-February and finally waning in April. During full five months the ground is frost-bound and heavily blanketed with snow. The coldest place in winter is Fort Kent, on the extreme northern border, where the thermometer frequently reaches as low as 40° F. below zero (—40° C) and the mean annual temperature is 37° F. (+3° C.), and the coolest place in summer is probably the sentinel city of Eastport, with a mean summer temperature of 59° F. (19° C.). Portland enjoys a mean annual temperature of 46° F. (8° C.), and the influence upon the climate of this city by the sea of the Arctic current, of which I have spoken, may be inferred from the presence in the waters of Casco Bay of those delicate Arctic pteropoda, the clionidæ, in enormous numbers.

With no mountains of excessive height—the loftiest, Katahdin, reaching an elevation of only 5,385 feet (1,647 m.)—and these arranged as isolated peaks, rather than in chains; with an average

elevation above sea level for the whole State of something like 600 feet (183 m.), and ranging from 5,200 feet (1,600 m.) down to sea level; with a surface consisting essentially of two great plateau-like slopes, the more extensive facing to the south and draining into the Atlantic, the lesser facing northward and draining into the St. John River; with practically half of its entire territory still heavily forest-clad, uncleared, unsettled and in many respects unknown except for its mantle of living green; gemmed with more than 1,600 bodies of inland water sufficient in size to be denominated lakes, or one lake to every 20 square miles (55 sq. km.) of territory and one square mile of lake surface to every 14 square miles of land surface; laced with more than 5,000 streams of pure and limpid water; with five great drainage basins collecting and conveying seaward the trillion and a quarter cubic feet (thirty-five billion cu. m.) of water annually discharged from its surface by its rivers, Maine may well justify its proud and oft-repeated boast that no other tract of country upon the North American Continent is equally well watered.

Assuming the annual rainfall at an average of 42 inches (107 cm.) over the entire breadth of the State, it has been computed that it would aggregate more than three trillion cubic feet (eighty-six billion cu. m.). The estimated annual discharge by river systems given above is thus clearly seen not to be excessive, as it constitutes but 40 percent of the total precipitation. This computation allows a diurnal discharge of water-power material exceeding three and one-third billion cubic feet (eighty-six million cu. m.). Falling through an average descent of 600 feet (183 m.), this discharge, could it be utilized to the full, would supply a working energy of more than two and a half million horse-power.

Upon the basis of these figures, if the reasoning so far is sound, it will be readily apprehended that, from one standpoint at least, Maine's chief advantage for the development of electro-chemical industries consists in her wonderful dowry of water-power resources. The statements hitherto made support the opening postulate of this paper so far as concerns geographical and meteorological conditions. But geology plays no mean or subordinate part in the problem of the proper development and

conservation of these resources, as well as in demonstrating how phenomenally nature has blessed the State in their regard.

As a general proposition, it may be accepted that the rock formations of Maine are among the most ancient, with a few exceptions either antedating in the period of their formation the appearance of terrestrial life, or, where the contrary is true, having been laid down so early after the introduction of life upon the globe that subsequent geologic events have nearly if not wholly obliterated the evidence of organic remains. The rocks of the State are therefore markedly characterized by non-permeability, induration and capacity to resist the action of erosive agencies. Rocks allied to granite underlie nearly one-half the entire area of the State. This makes practically every interior body of water in Maine a non-leakable, rock-bound, rock-floored reservoir, which can be relied upon to conserve in amplest measure its entire storage capacity over the full period of the year. It also assures permanency in the foundation of all structures such as dams, retaining walls, canals, sluices, powerhouses and factories erected for the purpose of enlarging the storage facilities or employing the power resources of the lake systems. The igneous rocks are not the sole contributors to the stability of the water-power resources of the State, for the enormous masses of definitely stratified rocks underlying more than half the surface area of Maine favor water retention and control of flow by their extreme hardness as well as by the fact that the strike of their stratification is directly across the course of the river currents. Folding and tilting have so inclined their exposures as to produce innumerable ridges and pitches in the river beds, causing steep and broken rapids, cascades and waterfalls to be of frequent occurrence.

Owing to the markedly notable height above sea level of Maine's principal lakes, the sources of all her greater rivers are found at comparatively high elevations. Thus Moosehead Lake, the inland sea of 120 square miles (350 sq. km.), which constitutes the headwaters of the Kennebec River basin, lies at an altitude of 1,023 feet (310 m.) above sea level, some of the tributaries which feed the lake rising at still higher points up to 2,000 feet (600 m.), and in one instance up to 3,000 feet (900 m.) above the coast line, making an average altitude nearly

equal to that of Lake Superior as the source of the St. Lawrence. The Rangeley Lakes, in which the Androscoggin rises at 1,511 feet (460 m.) above sea level, are very nearly as high as Lake Itasca, the source of the Mississippi. Chesuncook Lake, in the Penobscot River, is 900 feet (270 m.) above sea level, but the west branch of the Penobscot above this lake starts at an altitude of nearly 2,500 feet (750 m.). On the headwaters of the St. John River, the Chamberlain Lakes lie more than 900 feet (270 m.) above sea level. The Saco River takes its rise at an altitude of more than 1,800 feet (540 m.). Yet the drainage basins through which these rivers discharge their waters, as compared with the St. Lawrence or the Mississippi, are short and their water-power resources are compactly concentrated in conveniently accessible sections.

The Penobscot, from its extremest headwaters to the sea, traverses, with all its windings, less than 300 miles (500 km.), its main water-power section, from Lake Chesuncook to Bangor, falling 900 feet (270 m.) in some 120 miles (200 km.). Similarly the total length of the St. John River, from its remotest sources to the sea, is but 450 miles (750 km.), of which the upper half are in Maine. The Kennebec River, from Moosehead Lake to the sea, is but 155 miles (250 km.) in length, its principal water-power section being between Moosehead Lake and the capital city of Augusta, at the head of tide water, with a fall in excess of 1,000 feet in its 112 miles (300 m. in 185 km.) of length. The Androscoggin River system in its greatest length, from the sea to the uppermost sources in the New Hampshire hills, is less than 110 miles (185 km.), its chief water-power section, from Rumford Falls to the tide, being 75 miles (125 kw.), although it is in fact a water-power river in its whole length of 150 miles (250 km.) from the lakes to Brunswick. The Saco River flows through a drainage basin of less than 100 miles (165 km.), of which the lower two-thirds only are in Maine, and falls 450 feet (135 m.) from Fryeburg, on the New Hampshire State line, to tide water at Biddeford. The principal water-power section is from Hiram to Biddeford, 35 miles (60 km.), in which distance it falls through a slope of nearly 10 feet to the mile (5 m. to the km.).

These hastily compiled data will serve a useful purpose if

they have demonstrated that in her sources of supply of cheaply utilizable water-power, Maine extends to the electrochemist many desirable advantages.

Her other vast resources will be found amply supplementing her contributions to hydraulic and hydro-electric development.

It is regrettable that there has never been an exhaustive geological survey of the State as a whole. In the early thirties of the last century, Prof. Charles T. Jackson, of Boston, made a geological reconnaissance of a large area, in time extending over several years, and his reports, long since out of print, are remarkable for their accuracy of observation and of statement and for their comprehensiveness in view of the primitive conditions then governing transportation. In 1861 and 1862, Prof. C. H. Hitchcock made another reconnaissance which, coming as it did in the midst of the great crisis of the Civil War, and buried as its results were in the annual reports of the Commissioner of Agriculture, has never been appreciated or realized upon as its merits deserve. For the past ten years the State Survey Commission, of which I have the honor to be the present head, has been steadily collaborating with the United States Geological Survey in a hydrographic, topographic and geologic survey of the State which will ultimately result in the complete mapping of its entire area. Our appropriations, however, have been small and the work has been correspondingly handicapped.

Conditions have not favored the mineral development of the State to the extent which its varied and extensive metalliferous and non-metalliferous deposits deserve. Prospecting and exploitation of these resources have been practically prohibited by the segregation in private ownership of enormous land areas comprising the forested regions, upon which the owners, who, in the majority of cases, secured their original title from the State for mere pittances, have steadfastly pursued the short-sighted and selfish policy of permitting no operations, save those connected with lumbering, to be conducted. As there are no public lands, properly so-called, Maine's once imperial domain of wild lands having been reduced by a system of political pillage to a single township and a few public lots reserved for charitable and educational purposes, successful mining operations, even where ore bodies are known to exist, can be conducted only by securing

title through private purchase, for which the land barons usually disdain to treat. In the more settled portions of the State, however, where land holdings are broken up in smaller parcels, there are many known deposits of commercial importance which it is reasonable to expect the future will see more extensively developed and some of which need only the magic touch of electrochemistry to spring into immense importance.

The iron ores of the Mt. Katahdin region, which for several decades furnished an output of high-grade charcoal iron from a single blast furnace, are of unusual character in their freedom from sulphur and phosphorus. There is a belt of hematite iron ore extending northeastward though several Aroostook County townships, ending in the well-known deposits of Woodstock, New Brunswick, which, with the development of the Aroostook water-powers and the use of the electric furnace, may be counted upon as a future source of supply in commercial abundance, lime and other fluxes being at hand within convenient distance. The feldspar deposits of the State are well known and are increasing their output; and, in connection with their development, gem mining is assuming considerable importance. It is, of course, elementary knowledge that in the production of tourmalines of the highest quality, Maine leads the world. At Catharine Hill, in Hancock County, there is now under development what is confidently believed to be the largest deposit of sulphide of molybdenum on this continent, if not in the world. There is already exposed an enormous ore-tonnage of molybdenite, averaging 2 percent MoS_2, in a granite matrix which carries also gold and silver values of commercial importance as a concentrating proposition. Silver-lead-zinc ores are abundantly found, but have been sparingly worked, owing to inherent complexities which in the past rendered their reduction difficult and unprofitable. I believe electrostatic separation and electric furnace smelting can be made to spell prosperity for the developers of these properties. Maine's copper deposits are extensive, though not worked, and the occurrence at various points in the State of small bodies of tin ores supports a sincere belief which, in common with every geologist since Jackson, I earnestly share, that at some point in the State there will yet be discovered a tin deposit of commercial importance. Jackson early noted the presence of wolfra-

mite in the Blue Hill region as an indication of the presence of tin; cassiterite deposits occur in Kennebec County, and the whole mass of molybdenite-bearing rock at Catharine Hill carries a minute dissemination of tin in cassiterite crystals, as well as in the form of a native alloy with bismuth. Maine's immense quarries of granite, lime and slate are too well known to need comment. Platinum has been located in place in several localities, and graphite of good quality is found at numerous points in commercial abundance.

Add to these natural advantages the fact that all portions of the State are now fairly well served by lines of steam and electric transportation, that freight rates by overland routes are practically everywhere forced into competition with those for water-borne traffic, that vast tidal powers lie unimproved all along the coast, and that the agricultural capacity of the State is sufficient to support a population of millions, whereas to-day Maine, with less than 23 inhabitants to the square mile, is the least densely peopled of any Eastern State but Florida, and I believe there is made out at least a *prima facie* case that Maine offers opportunities and advantages for the development of electrochemical industries unsurpassable by any of her sister commonwealths.

Maine's invitation to both capital and labor is hearty, and should be attractive. Nowhere on earth can be found a more intelligent, more enterprising or more thrifty people than constitute her citizenry, and their hospitality to both the transient sojourner and the permanent settler is unfeigned and unstinted.

An Illustrated Lecture delivered at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 7, 1911, President Wm. H. Walker in the Chair.

ON THE RELATION OF SURFACE ACTION TO ELECTROCHEMISTRY.*

By Harrison E. Patten.

I wish to speak to you tonight on the interrelation of surface action (as influenced by surface tension) and electrochemistry.

Surface action is broad and far-reaching, and permeates in a fundamental manner all physical and natural science. Consequently, before entering upon even a general outline it is necessary to set straight our attitude toward the whole subject of cause and effect in physical science. This is the more needed at present because of a supercilious attitude toward "mere empirical facts or empirical experimentation," which has grown up in many of our sciences. The goal of some of our famous scientists has been and is to develop theories concerning the natural phenomena, rather than to connect these phenomena to each other in the relation of cause and effect. This same tendency may be stated slightly differently as a striving to explain phenomena, rather than to control and utilize these phenomena. Obviously, man can utilize if he can explain; the fallacy of this attempt to explain lies in the everlasting incompleteness of explanations put forth by man. The greater harm done by explanations lies in the satisfaction they give us. If someone has "explained" a certain phenomenon, we are likely to make no effort to investigate further its relation to the environment in which we find it.

The attempt to "explain" becomes hopelessly involved, too, when we enter, for instance, such a subject as electrochemistry, because so many sets of phenomena are operative in even the simplest systems. The set called chemical, that called electrical, and that called hydrodynamical are each explained by numerous theories dealing with their various individual actions. It requires patient critical skill for a specialist in any one of these subjects to

* Published by permission of the Secretary of Agriculture.

separate the operative facts from the theories, as they appear in text-books and in many research articles.

Consequently, even in this lecture which aims at correlation of basic facts, I am fully aware that some hypotheses may have run the mental blockade which I have tried to establish against them. One has only to read Henry Crew's essay* on fundamental concepts in physical science to become exceedingly careful before saying that all "theory" is eliminated in any treatment such as this. Passing now to the

General Phenomenon of Distribution.

When two phases touch, forming a boundary surface, a substance soluble in each of these phases will be divided between them.

This division of the solute is usually called *distribution.* The distribution may be equal, each phase holding one-half of the solute in solution, or, as generally happens, the distribution may be unequal.

The distribution of a solute between two phases is usually indicated by a ratio or fraction called the *distribution coefficient,* which gives the quantity of solute in one phase compared to that in the second phase. Thus, if two-thirds of the total solute present in the entire system (both phases taken together) be dissolved in phase *A,* and the remaining one-third in phase *B,* the distribution coefficient would be ½ or 1 : 2.

Effect of Concentration upon Distribution: The distribution of a solute between two phases may be related to its solubility in these phases, but this relation is not direct or simple—except insofar as the limit of concentration attainable in either of the phases is determined by the quantity of solute which remains dissolved in that phase when in contact with a solid phase of the solute itself.

More concretely stated, this means that while a distribution ratio of 2 : 1 may be observed for a solute between, say, ether and water, when one gram of solute is present in the total system, a different distribution may be and probably will be found when more or less solute is present in the total system.

* Science, 31, 521 (1910).

Distribution Curves: By plotting the quantity of solute in solution per unit volume in one phase as abscissa, and the quantity of solute per unit volume in the second phase as ordinate, on rectangular co-ordinate paper, a curve is obtained which expresses the distribution for all quantities of solute (between *O* and the limit imposed by solubility) which can be added to either phase under consideration.

Linear Distribution: Where such a distribution curve is a straight line, *i. e.,* where the total quantity of solute present in the two phases taken together does not change the distribution ratio, the distribution of this solute between the two phases is called linear.

Exponential Distribution: Usually variation of the total quantity of solute present in the system produces a marked variation in the distribution coefficient and the curve found upon plotting the distribution of solute between phases may frequently be expressed as an exponential function; thus $C^n/C_1^m=K$, where C is the concentration in phase A, C_1, the concentration in phase B, K a constant for given temperature and pressure, and n and m are exponents (fractions or integers), so chosen as to fit the experimentally determined distribution curve and thus permit us to describe it in concise algebraic form.

Distribution between more than two phases: This style of distribution has generally been considered not as such, but rather given under other names in studies—especially equilibria studies involving contact of three and more phases.

Having thus laid down the fundamental concepts of distribution, I will outline in brief the main points to be presented in the treatment which follows: first, a discrimination between surface tension and surface energy; second, a presentation of the fundamental equations for surface tension relations in general as derived by J. Willard Gibbs; third, extension of these equations to the case where the surface bears a charge of electricity; fourth, application of these general and fundamental equations where the surface bears an electrical charge, to the migration of suspended particles (solid, liquid, or gas); fifth, a discussion showing the intimate relation of this migration phenomenon to so-called electric osmose; sixth, further, that the subject of surface tension

deals with the so-called disperse systems, such as sols, where all of the suspended particles are held up far apart from each other in the liquid medium, and the so-called jels, where the particles are much more closely bound together by the liquid medium; and finally, seventh, a discussion of the bearing of the foregoing treatment upon the formation of electrolytic deposits, and conversely upon the corrosion of electrodes.

Equations for Surface Energy in General.

J. Willard Gibbs developed his formula for surface action entirely in terms of energy, mass, and temperature, making no assumptions as to the constitution of matter. First he takes a surface of no curvature, and shows that any energy change which takes place due to a heaping up of solvent and of any number of solutes is equal per unit area to the entropy change plus the product of each small excess mass in the surface layer, multiplied by its own chemical potential $\left(\frac{d\epsilon}{dm}\right)$

Thus

$$\delta\epsilon = t\delta\eta + \mu_1 dm_1 + \mu_2 dm_2 + \mu_3 dm_3 \qquad (1)$$

Then considering the same equation as applied to a curved surface, it is necessary to introduce another term, $\sigma d\omega$, in which σ is a force, and $d\omega$ is the change in surface (stretching or contraction), which causes the variation in the potential energy resident in the surface film to manifest itself (as $\sigma = d\epsilon/d\omega$).

The fundamental equation for heterogeneous systems given by Gibbs is

$$d\epsilon = td\eta - pdv + \mu_1 dm_1 + \mu_2 dm_2 \qquad (2)$$

etc., where temperature and pressure and chemical potentials are held constant, and volume, entropy and reacting masses vary.

The equation

$$d\epsilon^s = td\eta^s + (\sigma d\omega)^s + \mu_1 dm_1 + \mu_2 dm_2 \qquad (3)$$

shows the *analogy of surface tension to pressure,* on comparing it with equation (2). In this equation, temperature, surface tension and chemical potentials are maintained constant, while surface, entropy and the masses of solvent and solute,—which heap up in excess in the surface film,—vary.

For the purpose of securing an expression showing how the variation of surface tension, temperature and chemical potentials affect the masses of solvent and solute in the surface film, Gibbs integrates the equation (3) over the surface ω, and obtains:

$$\epsilon = t\eta + \sigma\omega + \mu_1 m_1 + \mu_2 m_2, \text{ etc.} \qquad (4)$$

Then he holds ω and ϵ, and η and m_1, m_2, constant, and varies μ_1, μ_2, σ and t, which gives:

$$0 = \eta dt + d\sigma\omega + d\mu_1 m_1 + d\mu_2 m_2 \qquad (5)$$

Then he divides by ω to get an expression for each unit area,

$$0 = \eta_s dt + d\sigma \times (1) + d\mu_1 \Gamma_1 + d\mu_2 \Gamma_2 \qquad (5a)$$

where $\Gamma_1 = m_1/\omega$ and $\Gamma_2 = m_2/\omega$. Rearranging,

$$d\sigma = -\eta_s dt - d\mu_1 \Gamma_1 - d\mu_2 \Gamma_2 \qquad (6)$$

Here it should be remembered that $d\sigma$ is $d\sigma \times$ unit area, and is a work, not a force.

We will consider now the difference between surface energy and surface tension. In many of our published researches, and in many of the text-books, the statement is made that surface energy is numerically equal to surface tension, and in the fundamental equation [(6) above] for adsorption effects, Gibbs expresses it in just that way; he has multiplied the surface tension into an area, which, of course, gives the work. The trouble is, men begin correctly, and then pass gradually into a use of surface tension as surface energy, and the result is very confusing. I wish to point out that in the adsorption equation (6), which is usually given with all the research articles on adsorption, $d\sigma$ really is an area multiplied into the surface tension. Further, the equation (6) shows that at constant temperature the rise in surface tension $d\sigma$ is proportional to the decrease in excess solute in the surface layer multiplied by its increment (negative in this case) of chemical potential—provided no heaping-up of solvent takes place in the surface film.

Another way of stating this relation is: Substances which lower the surface tension are adsorbed, while, conversely, those which raise the surface tension are negatively adsorbed.

In order to obtain an expression for the chemical potential

change $d\mu$ in the last equation (6), which contains physically measurable quantities, a differential equation

$$\frac{\delta\sigma}{\delta v} = -\frac{\delta p}{\delta\omega} \qquad (7)$$

has been developed,[1] using the customary cyclic process of thermodynamics.

This equation states that the surface tension varies with the volume, but the concentration enters only implicitly (since it

[1] Assumptions:

1. That the gas phase contains no vapor of the solute, but only vapor of the solvent.

2. That the gas phase contains a second vapor, such as air, which is practically insoluble in the liquid phase.

3. That the cyclic process used is actually a reversible one.

These conditions obtain for most systems actually met in practice, though of course not in a strict sense.

Let the volume of the solute be v
" " concentration of solute be c
" " osmotic pressure be p
" " surface—*total*—be ω
" " surface tension be σ

(a) Now, using the cyclic process, let the surface ω be increased to $\omega + d\omega$, this uses the work $-\sigma d\omega$, while v, the volume, remains unchanged, but the osmotic pressure is changed to the value, $(p + \delta p/\delta\omega . d\omega)$.

(b) Increase the volume to $v + dv$; this sets free the work $(p + \delta p/\delta\omega . d\omega)dv$, while the surface $(\omega + d\omega)$ remains constant, but σ changes to the value $(\sigma + \delta\sigma/\delta v . dv)$.

(c) Now let the surface $\omega + d\omega$ shrink to ω, its former area, thus setting free the work $(\sigma + \delta\sigma/\delta v . dv)d\omega$, and the osmotic pressure, $p + \delta p/\delta\omega . d\omega$, goes back to its former value, p.

(d) Finally, let the volume $v + dv$ be decreased to its original value, v; this requires the work $-pdv$.

Since the cyclic process is isothermal, the sum of the work is zero; this gives by cancellation $\delta\sigma/\delta v = -\delta p/\delta\omega$.

This differential equation shows that the surface tension varies with the volume—or what is the same thing, with the concentration—if the osmotic pressure varies with the surface (*i. e.*, surface stretching,—mere addition of adjacent surface of liquid will not alter conditions, it merely makes a larger system to consider).

But this can be true only if the concentration of solute in solution depends upon the extent of surface of the solution. Let us see how σ depends upon c: c is a function of v and of ω. If the solution contains

depends upon the volume), so we further develop equation (7) as an explicit function of c.

$$\frac{\delta\sigma}{\delta c}\cdot\frac{\delta c}{\delta v}=\frac{\delta p}{\delta c}\cdot\frac{\delta c}{\delta\omega}\quad\text{Setting}\quad c=\frac{nu\,.\,\omega}{v}\qquad(8)$$

(where n is the number of gram molecules in volume, v, and u is the excess gram molecules of solute per unit area of the surface, ω) and performing the indicated differentiations.

$$c\cdot\frac{\delta\sigma}{\delta c}=-u\frac{\delta p}{\delta c}\qquad(9)$$

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n gram-molecules, then the concentration is not simply $c = n/v$, but rather, $c = n - u.\omega/v$, where u represents the excess or deficiency of solute in the surface layer over that in the bulk of the solution, for *each unit area of surface.*

Take now the equation $\delta\sigma/\delta v = -\delta p/\delta\omega$, and develop it as a function of c, and we obtain $\delta\sigma/\delta c.\delta c/\delta v = -\delta p/\delta c.\delta c/\delta\omega$, but, as just shown, $c = n - u.\omega/v$, so $\delta c/\delta v = n - u.\omega/v^2$; and differentiating with respect to ω, $\delta c/\delta\omega = -u/v$.

Substituting now these values of $\delta c/\delta v$ and of $\delta c/\delta\omega$, this equation says that the concentration multiplied by the change of surface tension with change in concentration is equal to the excess of solute in the surface layer per unit area, multiplied by the change in osmotic pressure with change in concentration.

Thus far only actually measurable forces and quantities have been considered. If now we assume the law $PV = RT$ for gases as applying to $\Pi V = RT$ for solutions, according to van't Hoff then $\delta p/\delta c = RT$, and $u = -c/RT.\delta\sigma/\delta c$.

Referring back to equation (6) [*i. e.*, $d\sigma = -\eta_s dt - \Gamma_1 d\mu_1 - \Gamma_2 d\mu_2$], if t is constant, and μ_1 is constant, $d\sigma = -\Gamma_2 d\mu_2$ where $\Gamma_2 = u$ by definition, consequently $u = -\delta\sigma/d\mu_2$. Equating now these two values of u, $d\mu_2 = RT\,dc/c$.

Milner's introduction of factor, i (S. R. Milner, On Surface Concentration and the Formation of Liquid Films, Phil. Mag., 6 *13*, 96 (1907)): If i stands for the ratio of the molecular lowering of the freezing point (lowering per gram molecule per liter) to the normal lowering 1.86, then $p = iRTc$, and consequently $dp/dc = iRT + RTc\,di/dc$. But since i varies only slightly with the concentration for dilute solutions, the term $RTc\,di/dc$ vanishes, and we have approximately $d\sigma/dc = -iRT\,u/c$.

In practically all inorganic solutions the surface tension (liquid-gas) increases linearly with concentration, so $d\sigma/dc$ is positive; hence u is negative and u/c is constant, namely, there is a *defect* of salt in the surface film of an amount proportional to the concentration.

In this equation, c, the concentration of the bulk of the liquid; $\delta\sigma/\delta c$ the change in surface tension as c is changed; u the excess of solute per unit area of surface film; and $\delta p/\delta c$ the change in osmotic pressure with change in concentration, are all (more or less accurately) measurable quantities. But the expression for $d\mu$, the change in chemical potential, has not yet been obtained.

By applying the gas law to solutions, *but making no assumption as to the state of matter in solvent or solute,*

$pv = iRT$ where p is the osmotic pressure, (10)

" v is the volume of solution,

" i is a factor which varies slightly with the concentration,

" R is the gas constant, approximately 2, and

" T is the absolute temperature. Then

$$\delta p/\delta c = iRT \text{ since } c = n/v \text{ or } v = n/c; \qquad (11)$$

and here, in (10), n, the number of gram molecules of solute, is taken as one.

Substitute in equation (11) this value, $\delta p/\delta c$ and we obtain

$$u = -\frac{c}{iRT} \cdot \frac{\delta\sigma}{\delta c} \qquad (12)$$

This expression is useful by itself, but still does not give us the value of $d\mu$. For this purpose, refer back to Gibbs' fundamental equation (6), $d\sigma = -\eta_s dt - d\mu_1\Gamma_1 - d\mu_2\Gamma_2$. If temperature is constant, and there is no excess solvent in the surface film, this reduces to

$$d\sigma = -d\mu_2\Gamma_2 \qquad (13)$$

(Γ_2 is the same as u, by definition), or $d\mu_2 = -u/d\sigma$. Substitute the value of u given in (11), and

$$d\mu_2 = iRT\frac{dc}{c} \qquad (14)$$

It should be remembered in using the factor i that we are assuming nothing whatsoever as to the relevancy or irrelevancy of the theory of electrolytic dissociation. The factor i is an ex-

perimentally determined quantity, and has nothing to do with the theory one way or the other—it is just as much an actual quantity as the other factors.

Equations (12) and (14) enable us to compare intelligently the variable factors involved in surface changes at the boundary between a liquid and a gas.

In this connection it should be shown how the surface tension and vapor pressure are related: Using a cyclic process,[2] it can be shown that

$$p\omega = p + 2\sigma\rho_g/\rho_1 . r \qquad (15)$$

Where $p\omega$ is the vapor pressure at the surface of a drop, and p the pressure over the free plane surface of the same liquid; ρ_g and ρ_1 the densities of the gas and liquid respectively; r is the radius of the drop.

Further, the quantity of heat set free when one gram of liquid in drop form, of radius r, is carried over into a flat liquid surface is

$$Q = \frac{2}{\rho . r} . T \frac{d\sigma}{dT} \qquad (16)$$

Where r is the radius of the drop, and ρ is its density at the absolute temperature, T, $d\sigma/dT$ is the rate of change of surface

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[2] SURFACE TENSION AND VAPOR PRESSURE.

(Reversibility is postulated in this cyclic process.) Using a cyclic process: let two drops of the same liquid have the radii r_1 and r_2. If we take the mass dm of the first drop and add it to the second drop, then the surface of the first drop gains work $\sigma d\omega_1$, and the surface of the second drop uses up work $\sigma d\omega_2$. The magnitude of $d\omega_1$, the change in area of the first drop, depends upon how much the area of the total surface changes with the weight of the drop. That is, $d\omega_1 = \delta\omega_1/\delta\omega_1 . dw_1$, where w_1 is the weight of the first drop.

Now since $4\pi r_1^2 = \omega_1$, the total surface of drop number 1, and $4/3\pi r_1^3\rho = w_1$ (ρ = density of liquid), $\delta\omega_1/\delta r_1 = 8\pi r_1$ and $\delta w_1/\delta r_1 = 4\pi r_1^2\rho$, that is, $\delta\omega_1/\delta w_1 = 2/r_1\rho$; consequently $d\omega_1 = 2/r_1\rho . dw$.

Similarly, for the change of surface of drop number 2, $d\omega_2 = 2/r_2\rho . dw$. Thus the surface work involved in transporting mass dm of liquid from drop number 1 to drop number 2 is $\sigma(d\omega_1 - d\omega_2)$ or $2\sigma/\rho\ 1/r_1 - 1/r_2)dw$. Now to complete the cyclic process, let the mass dm of liquid be distilled back from drop number 2 to drop number 1. The vapor pressure must be different at each drop's surface, p_1 and p_2. So the distillation work, as is well known, will be $RT\ln p_2/p_1 . dw$. Since the cyclic

tension liquid-vapor with temperature, at the given absolute temperature, T.

To make concrete the actual magnitude of the defect of solute in a surface, sodium chloride may be cited as an average case[3]: The increase of surface tension is 1.72 dynes per cm. for an increase of 1 gram molecule per liter.

Now i = 1.74 (taking an average value for the factor)

R = 8.32×10^7 ergs per degree C.

T = 290° (17° C.)

Substituting these in equation (12), $d\sigma/dc = -iRT\ u/c$. This is equal to a defect of 0.024 mgs per square meter.

Conversely, for a lowering of σ, the substance will concentrate in the liquid film.

This treatment of surface factors given by Gibbs[4] differs in a way from that given for systems in bulk, in that we must always have two different phases in contact to secure a surface of separation, whereas a system in bulk may consist of one homo-

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process is isothermal, the sum of the two work fractions must be equal to zero, $RT\ln p_2/p_1 + 2\sigma/\rho\ (1/r_1 - 1/r_2) = 0$, or $RT\ln p_2/p_1 = 2\sigma/\rho\ (1/r_2 - 1/r_1)$.

The term on the right is positive when $r_2 < r_1$, and in this case, $p_2 > p_1$; that is, the smaller drop has the greater vapor pressure.

The formula is simplified if we compare a drop with a plane surface of the same liquid; then the radius curvature of the plane surface, $r_1 = \infty$ and $p_1 = p$, the regular vapor pressure of the liquid at that temperature, and we have $RT\ln p_2/p = 2\sigma/\rho r_2$. If we put for p_2 and r_2 simply p_ω and r, we have by developing the left side $\ln p_\omega/p = \ln (1 - p\text{-}p_\omega/p) = (p_\omega/p - 1)$, thus obtaining $p_\omega/p - p = 2\sigma p/RT.\rho r$. Remembering that $p/RT = \rho g$ (since v is the volume containing a gram molecule and hence defines the density), this becomes $p_\omega = p + 2\sigma\rho g/\rho_1.r$; which shows how much greater the vapor pressure at the surface of a drop is than that over the free plane surface of the liquid. This holds for a convex surface. For a concave surface the vapor pressure is correspondingly smaller. According to Carnot's law, the quantity of heat which is set free when one gram of a liquid in drop form, whose radius is r, is carried over into a flat liquid surface, $Q = 2/\rho.r\ .\ T\ d\sigma/dT$.

If a drop has a radius of 0.001 mm., its vapor pressure is 1 part in 1,000 greater than that over the flat surface of the liquid. (See Freundlich, Capillar Chemie., p. 46.)

[3] S. R. Milner: Phil. Mag. [6] **13**, 98 (1907). See also Wm. C. McC. Lewis, Ibid., [6] **17**, 466 et seq. (1909).

[4] Scientific Papers, Thermodynamics, p. 222, Longmans, Green and Company, 1906.

geneous phase, whose mass is constant, but whose volume, pressure, entropy and temperature may vary.

In considering adsorption, the surface may be between liquid and gas, liquid and solid, or gas and solid. The first surface, liquid-gas, is the one usually measured. The second, liquid-solid, is the one most concerned in adsorption, and *we know least about it!*

ELECTROCHEMICAL ASPECTS OF SURFACE ACTION.

For the capillary electrometer,[5] let

ω = surface mercury-electrolyte

σ = surface tension (a force)

ϵ = electrical potential

e = charge of electricity on surface ω

[e] charge of electricity per unit area of surface mercury-electrolyte = $de/d\omega$.

I. Using the cyclic process, let us increase the surface ω (Fig. 1) to $\omega + d\omega$ (Fig. 3). This requires the work $\sigma d\omega$ to be done, which is expressed negatively $-\sigma d\omega$, since work is put in. The charge e remains the same, but the electrical potential ϵ is diminished to $\epsilon - \delta\epsilon/\delta\omega\ d\omega$ (Fig. 4).

II. Now increase the charge by de, and thus put in work $-(\epsilon - \delta\epsilon/\delta\omega\ d\omega)\ de$. In this operation, the surface $\omega + d\omega$ is not changed, but the surface force σ is changed to $(\sigma + \delta\sigma/\delta e\ de)$.

III. Let the surface mercury-electrolyte now return to its former area ω; this releases the work $+ (\sigma + \delta\sigma/\delta e\ de)\ d\omega$.

IV. Finally, withdraw from the surface which has again assumed the potential ϵ, the charge de, and release the work $+\epsilon de$ (Fig. 4). Since the sum of the four work terms must be zero, $-\sigma d\omega - (\epsilon - \delta\epsilon/\delta\omega\ .\ d\omega)\ de + (\sigma + \delta\sigma/\delta e\ de)\ d\omega + \epsilon de = 0$, which reduces to

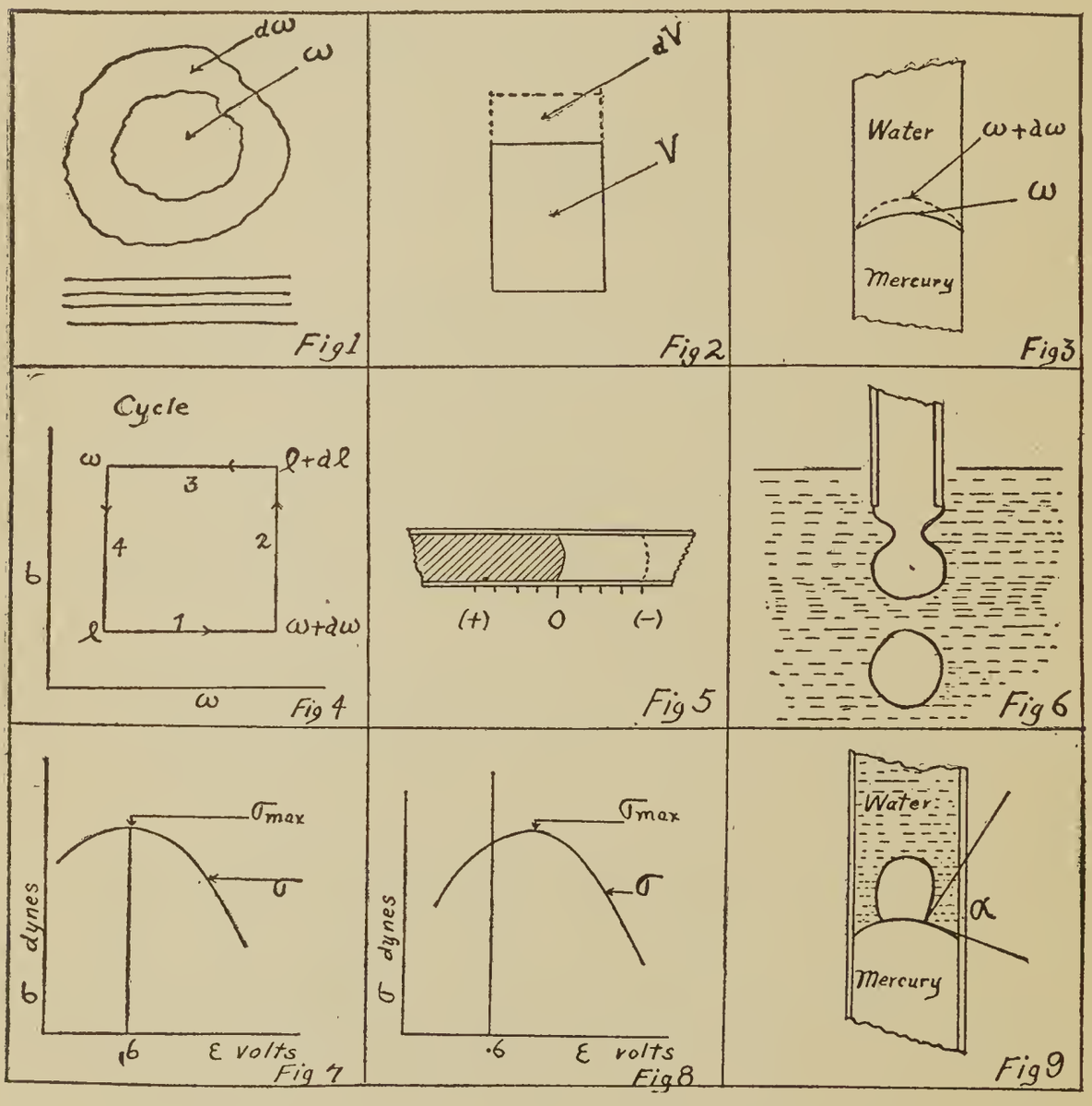
$$\delta\sigma/\delta\epsilon = -\delta e/\delta\omega = -[e] \qquad (17)$$

where by definition [e] is the charge of electricity per unit area.

The maximum comes when $[e] = 0$, *i. e.*, when there is no charge on the mercury-electrolyte surface (Fig. 5).

[5] Freundlich, Kapillarchemie., p. 186.

In this treatment for the capillary electrometer, the interface between two different liquids, mercury and an aqueous solution, has been taken (Fig. 5), whereas the preceding treatment has dealt with the boundary surface between a vapor and a liquid. If we could measure the surface tension between frozen water and mercury, it would give us a measurement on the surface



tension solid-liquid which is of supreme importance in studying adsorption effects. By working very close to the solidification temperature, we might exterpolate, but this is merely a suggestion.*

Fig. 6 illustrates the case of the dropping electrode, where mercury passes through an electrolyte and the fresh mercury

* cf. Wm. C. McLewis. Zeit. Ind. Koll. **5**, 91 (1909).

surfaces are formed so fast that they have not time to adsorb sufficient of the dissolved salt to produce the potential which they maintain against the electrolyte under equilibrium conditions. Consequently their potential remains that of the surrounding solution, and by using a dropping electrode opposed to a quiescent mercury electrode, such as shown in Fig. 5, we obtain an electrical difference of potential, due solely to the mercury-electrolyte interface which is in a steady state. In Fig. 7 the change in surface tension at the surface mercury-electrolyte produced by an increase of electromotive force applied from an external force is given. It will be noticed that the surface tension passes through a maximum at about 0.6 of a volt, which corresponds with the difference of potential of mercury against the electrolyte (this value, 0.6 volt, is given merely for illustration and does not refer to any particular substance in solution).

The position of this maximum surface tension on the σ-ϵ curve varies with the amount of acid (or other dissolved body) and with the chemical nature of the dissolved substance, as the diagram given in Fig. 8 indicates. This σ-ϵ curve may be represented by the equation,

$$\sigma_{max} - \sigma = q/2\epsilon^2, \text{ a parabola, where } de/d\omega = [e] = q.\epsilon. \quad (18)$$

Much work has been done using the interface of various liquids which are either immiscible or only partially miscible. A modification of this electrocapillary method is the case where a bubble of gas is in contact in part with the mercury and in part with another liquid which touches the mercury, as shown in Fig. 9.[6]

Using the equation

$$\sigma_{Hg}' - \sigma_{Aq}' = \sigma_{Hg-Aq} \operatorname{Cos} \alpha \quad (19)$$

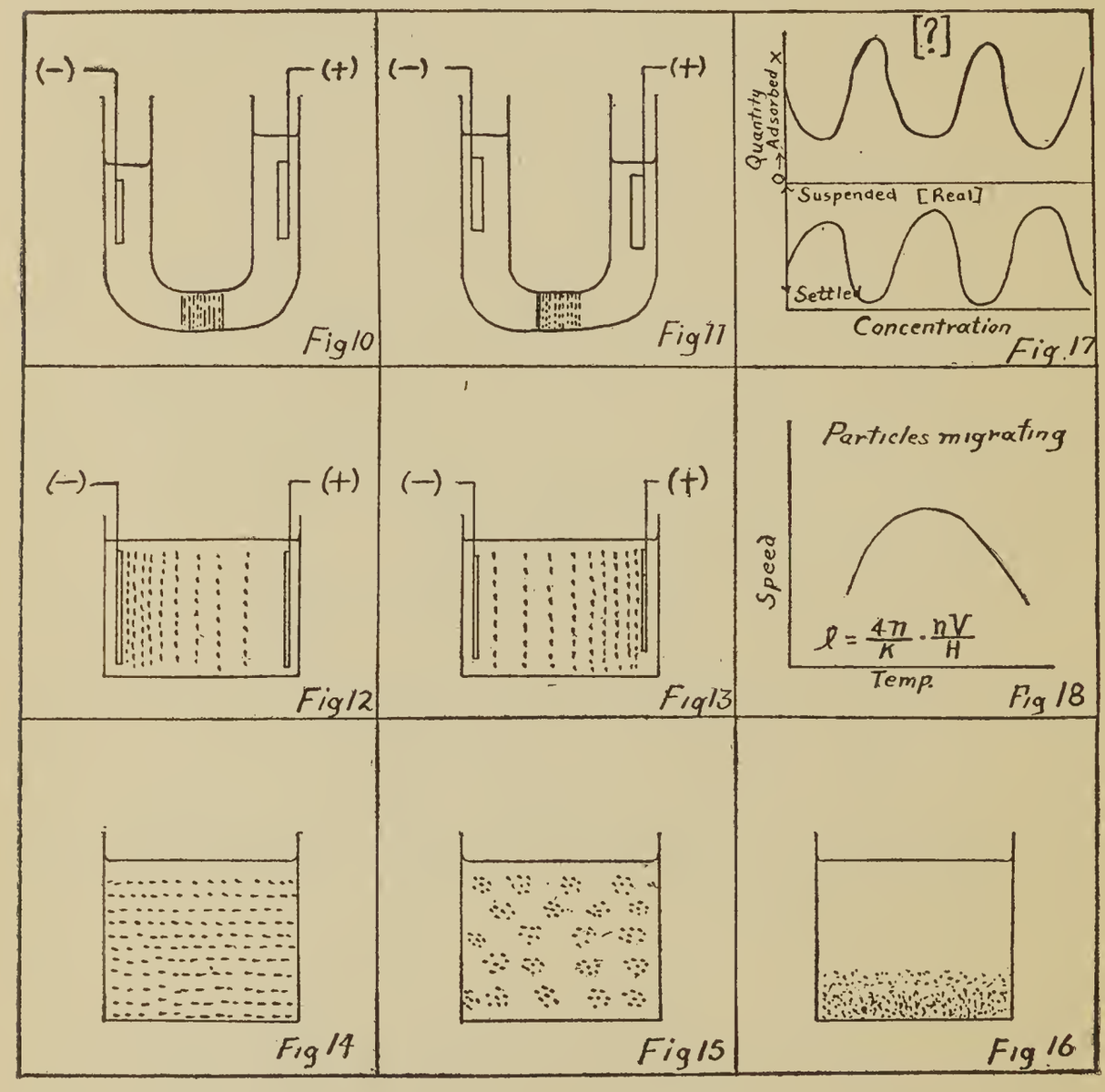
the angle α may be used as an indicator for the voltage. Thus Möller found for α maximum that the bubble method gave —0.76 volt for mercury; —0.76 for nickel; —0.77 for copper; and —0.76 for silver in 0.1 n. sulphuric acid.

Having now discussed the general equations of surface tension and their application to two forms of the capillary electrometer and to the dropping electrode, let us consider the relation of

[6] C. Christiansen, Ann. der Physik., [4] **12**, 1072, et seq. (1903. Möller, Zeit. phys. Chem., **65**, 248 (1908).

surface tension to electrical osmose, and to the migration of suspended particles under potential difference.

When a diaphragm is introduced between the anode and cathode chambers of an electrolytic cell, during electrolysis an increase of the volume of liquid in the anode chamber is observed under some conditions, and under other conditions the volume of liquid in the cathode chamber increases. The direction of the



flow of electrolyte through the diaphragm is controlled by the chemical nature of the material in the diaphragm, the solvent and solute constituting the electrolyte, and the concentration of the solution (electrolyte) used in the cell. With a plug of one substance, osmosis in the direction shown by Fig. 10, toward the anode, will be obtained. With a plug of another material, the electrical osmose may be toward the cathode, as shown in Fig. 11.

Another aspect of the same phenomenon is exhibited by particles of solid, liquid or gas suspended in a liquid medium, as shown in Figs. 12 and 13. When an electromotive force is applied to electrodes immersed in such a suspension, the particles therein are seen to move toward one of the electrodes, and the liquid near the other electrode is gradually cleared of these particles. Under some conditions the particles migrate to the cathode, and under others to the anode, their direction being controlled by the chemical nature of the particles, the nature of the suspending liquid, and the concentration of soluble material in the suspending liquid, exactly as in the case just cited for electrical osmose.

To more directly correlate this migration of particles with electrical osmose, let us consider for a moment the settling and aggregation of suspensions. Figs. 14, 15 and 16 indicate the aggregation of suspended particles and their gradual compacting into a settled-out mass which is very comparable to that of the plugs used in the U tubes shown in Figs. 10 and 11. These same particles, as shown in Figs. 12 and 13, when free to move, travel through the liquid under stress of an electromotive force, but when wedged together, as in Fig. 16, into a plug, are not free to move, and the liquid being capable of motion, the stress produced by the electromotive force applied as in Figs. 10 and 11 is relieved by the movement of liquid past comparatively stationary particles. Thus it is seen that migration of particles and electrical osmose are essentially expressions of the same phenomenon.

The relation of adsorption to the migration of particles has been referred to previously, in connection with the capillary electrometer and the dropping electrode. The influence of the layer of adsorbed material (on the surface of suspended particles) upon the direction in which these particles will migrate in an electrical field is by no means thoroughly understood. It is, however, definitely connected with the phenomena of settling and resuspension of these same particles, as shown in Fig. 17. Buxton,[7] Teague,[7] Bechhold[8] and others[8] have shown that small additions of some soluble bodies will cause a suspension to

[7] Zeit. phys. Chem. **57**, 64 (1906); **57**, 76; **60**, 469, 489 (1907); **62**, 287 (1908).

[8] Ibid., **48**, 385 (1904); cf. Matthews, Am. Jour. Physiol. **14**, 203 (1905); Buckingham, These Transactions, **9**, 261 (1906); Patten, Ibid.,; Free, Jour. Franklin Inst.. etc.

settle; a further addition of the same solute will produce a resuspension, which upon still further addition of solute settles again. In some instances, as the concentration increases, the particles alternately go into suspension and again settle, as shown by the curve in Fig. 17; and numerous experiments have shown that the direction in which the particles migrate in an electrical field alternates from anodic convection to cathodic convection with increase of concentration, keeping pace with the settling and resuspension phenomena.

If this alternation of the relation between the suspended particles and the liquid medium is due to the quantity of adsorbed solute on the surfaces of the particles, we would at first sight expect to find that the distribution curve for this solute between liquid and solid particles alternately increased and decreased to keep step with the alternation of convection and the alternation of settling. Buxton, Teague and others (see reference) claim that this is the case for certain solutes which they have studied.[9]

Further, where the particles in suspension gradually dissolve in the liquid, there comes a gradual drop in the migration speed until in some cases a neutral point is reached, just before they are entirely dissolved, where the particles move neither to anode nor to cathode (Fig. 22). Gee and Harrison[10] give general equations for the relation of charge upon the surface of a porous plug to the rate at which the liquid filters, and also to the rate of migration of suspended particles.

Let K = dielectric constant
η = coefficient of viscosity
v = rate of liquid flow or speed of particle
q = equivalent cross-section of pores in diaphragm
H = strength of electrical field
E = e. m. f. produced
e = contact potential difference between liquid and solid
p = mechanical pressure (for filtration)
ρ = specific electrical resistance. Then

[9] cf. Absorbtion by Soils, and literature given, Bull. 52, U. S. Dep. Agric., Bureau of Soils. (1908); also Bull. 30, Ibid. (1905) Cameron and Bell; also Bull. 61 (1910) Ibid. Davis and Bryan.

[10] Trans. Faraday Soc. 6, 42, et seq.

$$e = \frac{4\pi}{K} \cdot \frac{\eta}{q} \cdot \frac{v}{H} \qquad (20)$$

In this case we measure rate of flow of liquid through diaphragm. If current be measured, q may be eliminated,

$$e = \frac{4\pi}{K} \cdot \frac{\eta}{\rho c} \cdot v \qquad (21)$$

Where we measure difference of electrical pressure between two sides of a diaphragm when liquid is filtered under mechanical pressure,

$$e = \frac{4\pi}{K} \cdot \frac{\eta}{\rho} \cdot \frac{E}{p} \cdot \qquad (22)$$

The mechanical pressure used in filtration is measured for equation

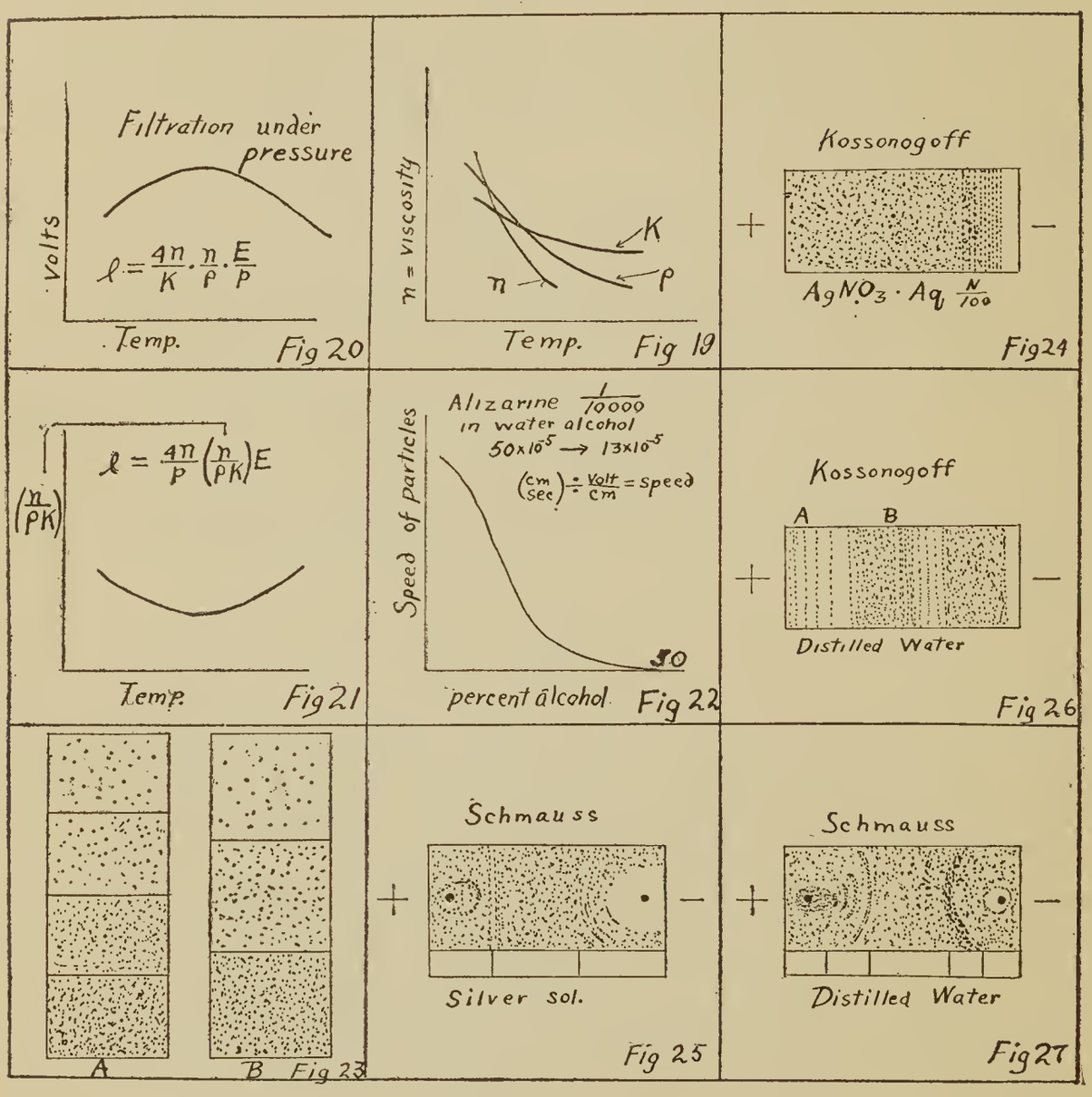
$$e_v = \frac{4\pi}{K} \cdot \frac{\eta}{\rho p} \times (3 \times 10^{10})^2 \qquad (23)$$

and for equation (24) we measure speed of particles (in suspension):

$$e = \frac{4\pi}{K} \cdot \eta \cdot \frac{v}{H} \qquad (24)$$

One would expect that the effect of temperature upon the migration of suspended particles in an electrical field would be in one direction,—either an increase or a decrease in the migration rate; but the experimental fact is that the speed of migration goes through a maximum as temperature increases. In the work of Gee and Harrison, cited above, they have shown that this maximum is (see Fig. 18) due to a difference in the temperature coefficient of three variables (viscosity, specific gravity, and dielectric constant), as shown in Fig. 19. The curve of filtration under pressure for the impressed voltage as a function of the temperature also shows the maximum (Fig. 20). Inspection of equations 22 and 24 shows the interrelation of these three quantities, viscosity, density, and dielectric constant, which $(\eta/\rho k)$ goes through a minimum as the temperature increases (see Fig. 21); and since this factor $(\eta/\rho k)$ enters into reciprocal relation to the speed of migration and to the impressed electro-

motive force used in filtration, the maximum observed in Figs. 18 and 20 necessarily follows. The effect of the solution process upon the migration of particles gradually dissolving is shown for a solution of alizarine 1/10000 in mixtures of water and alcohol. The alizarine dissolves completely in a percent of alcohol somewhat higher than 50. Below this percent of alcohol,



the alizarine forms a so-called colloidal suspension. The speed of migration of these particles when plotted against the percent of alcohol present in the suspended medium gives the curve shown in 22, according to Gee and Harrison.

In this connection a concise survey of the fundamental knowledge concerning Brownian movements and their bearing upon the settling of suspensions is in order: (1) The movement is appar-

ently independent of external sources of energy, and (2) independent of magnitude and sign of electrical charge on particle (Svedberg), (3) *Amplitude* = time of vibration × a constant (∴ movement is not "elastic"). (4) $A = k/\eta$ where A = amplitude, η = viscosity, k = a constant. (5) Speed is independent of "solvent" (Svedberg). (6) $(\text{Speed})^2 \propto$ temperature (F. M. Exner). (7) Speed $\propto$ 1/diameter (Exner). (8) Diameter of ultra-microscopic particles 1/100 of microscopic particles (Svedberg). (9) Speed $\propto$ concentration of particles in suspension (Zsigmondy). Stokes' law,

$$v = 2/9.D\text{-}d/\eta.Kr^2 \qquad (25)$$

holds for particles 0.14μ to 0.45μ where v = speed of settling, η = viscosity, k = force which produces settling (weight), D density of particle, d density of liquid (medium), r radius of particle.

J. Perrin has compared values of the diameter of particles of rubber (gummi gutt) by the methods of (1) actual counting with a microscope, and by (2) settling, using Stokes' law, and by (3) micrometrically determining the diameters. The three methods gave results as follows:

By counting	By settling (Stokes' law used)	Micrometrically
0.46	0.45	0.45
0.30	0.29	0.30
0.212	0.212	....
0.14	0.12	....

The concentration of suspended particles for rubber (A) and for mastic (B) is shown in Fig. 23. These observations were made by putting the emulsion upon a microscope slide under a cover glass and counting the average number of particles in focus at various depths.

The cause of the Brownian movements is unknown. Some have attributed it to a bombardment of molecules of the suspending medium upon the surfaces of the particles. Einstein and Smoluchovski[11] have developed fundamental equations for the

[11] Einstein, Ann. Physik [4] **17**, 549 (1905), and literature; Ibid [4] **19**, 371 (1906); Zeit. f. Elektrochemie, **13**, 41 (1907); Smoluchovski, Ann. Physik [4] **21**, 756 (1906). See also Grundriss der Kolloidchemie, von Dr. W. Ostwald, 2 aufl., p. 256.

kinetics of a dispersed system which differ from each other by the factor 2.37; thus

$$\Delta = \sqrt{K \cdot \frac{RT}{N} \cdot \frac{t}{\eta r}} \qquad (26)$$

where Δ = average length of path of particle; K = a constant; R = the gas constant; T = the absolute temperature; N = number of particles formed by a gram molecular weight of the disperse phase; t = the period of vibration of the particle; η = the viscosity of medium; r = radius of the particle, *assuming spherical shape.* Smoluchovski, — $\Delta = 2.37\sqrt{K \cdot \frac{RT}{N} \cdot \frac{t}{\eta r}}$

Applying the ultra-microscope to the study of migration in solution, J. J. Kossonogoff* has studied the electrolysis of a solution of 0.01 n.A_9NO_3 in water. As indicated in Fig. 24, he finds a stratification of points of light passing from cathode to anode, and is inclined to attribute this occurrence to a stratification of the ions as they are migrating. Schmauss found a similar stratification for a suspension of silver (silver sol) as shown in Fig. 25. Kossonogoff likewise found a stratification using distilled water, as shown in Fig. 26, which again is comparable to the result found for distilled water by Schmauss, Fig. 27. W. Ostwald† attributes this stratification of points of light observed by Kossonogoff to very fine particles of metal *as such* forming sols, rather than to ions. This contention is supported by the well-known experimental fact that metallic mercury is dissolved by water.‡ This suggests a relation between this stratification observed by Kossonogoff and the formation of metal deposits under the influence of electricity, because we may have these very fine centers acting as nuclei for aggregations which tend to migrate. Thus all the action will not take place at the cathode, but the particles may gradually increase, and finally begin to plate out at the cathode. The deposits of silver obtained in studying the silver coulometer[12] show clearly that more than one form of silver comes down at the

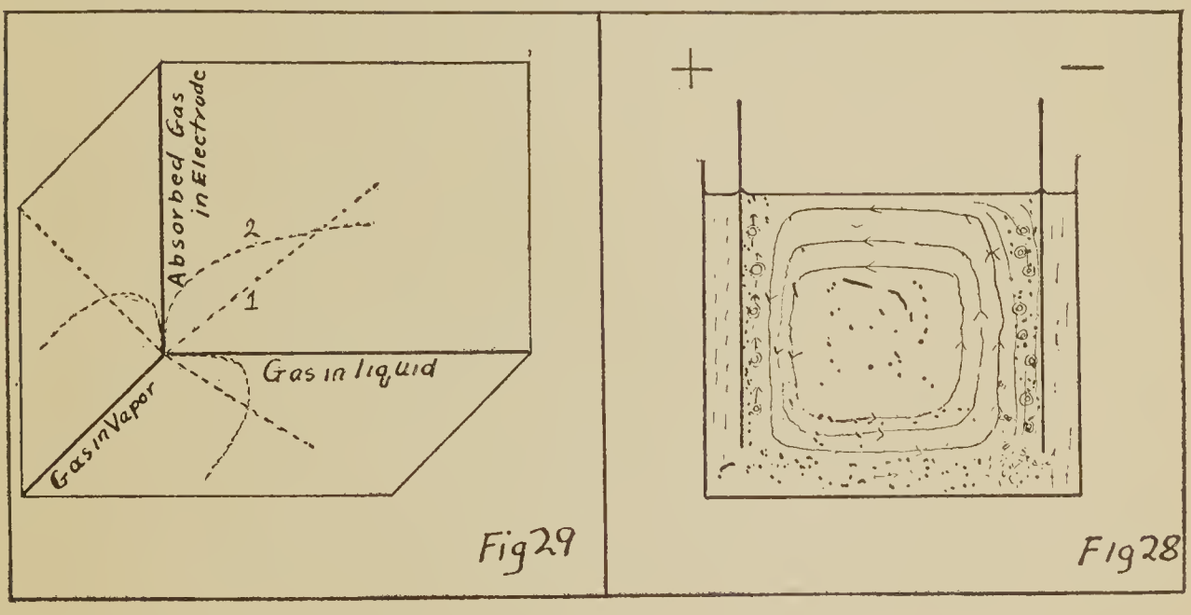
* Jour. Russ. Phys. Chem. Gess. **41**, 373 Jan. 1909. Physik. Zeit. **10**, 976 (1909); Zeit. Ind. Koll. **7**, 128 (1910).

† Zeit. Ind. Koll. **7**, 132 (1910).

‡ Traube-Mengarini and Alberto Scala. Zeit. Ind. Koll. **6**, 65 and 240 (1910).

[12] Rosa, Vinyl and McDaniel, Bureau of Standards Publications on the Coulometer.

cathode, a crystalline form and a form apparently produced by chemical reduction in solution and migration to the cathode, where it serves as an extension of the cathode and produces rounded and other odd forms of deposit. The inclusions of liquid, gas, etc., found in metallic deposits[13] confirm the view which is now generally held, that the deposition of metal at the cathode is a very complex process.[14] The converse of this deposition at the cathode and the many surface factors cited above which enter in to determine its character is observed at the anode where the metal passes into solution and into suspension. Fig. 28 illustrates roughly the conditions of cir-



culation and deposition which obtain at cathode and at anode during electrolysis.

The part which adsorption plays in consideration of residual currents may be touched upon here principally to indicate that in general the treatment usually given, which considers the mechanism of the residual current as a diffusion problem,[15] assumes that the quantity of gas contained in the electrode is directly proportional to the quantity of gas dissolved in the solution (in the linear relation). This in general is not found experimentally to be the case, as indicated in Fig. 29. The quantity of gas retained in the metal (or on it) is a function

[13] See especially the work of Hulett and the literature given by Patten, Trans. Amer. Electrochem. Soc., **11**, 398 (1907).

[14] See papers by C. F. Burgess, Mott, Hambuechen, Kern, Betts, Herring, Northrup, Goodwin, Richards and Ellis, Trans. Amer. Electrochem. Soc., **1-17**.

[15] H. Daneel, Zeit. f. Elektrochem. **4**, 211 and 227 (1897).

of the gas dissolved in the electrolyte, which in turn is a function of the concentration of gas in the vapor phase above the electrolyte (or in it) in the form of gas bubbles.

Before closing, let me refer to the very interesting work of Lille at Johns Hopkins University on the osmotic pressure of colloid suspensions. He was able to show that particles of albumen suspended in water have by no means lost their power to attract more water to themselves. By enclosing the suspension in a membrane, through which water could pass, but not the albumen particles, he showed that the pressure inside the membranous sack rose with time, the sack being immersed in a beaker of water. Further, by adding small quantities of various salts, acids and alkalis, he showed that there was a marked effect produced upon the magnitude of this osmotic pressure which evidently was due to the state of aggregation of these particles of albumen being affected by the added salt in solution. Conversely, it has been shown that the presence of salts in water affects the swelling of jell-like bodies such as fibrin in a manner which could be predicted from the experiments of Lille upon the osmotic pressure of these colloids. It thus appears that a particle completely surrounded by a suspending liquid medium still exerts a strong attraction upon that medium even after the major portion of its attraction for the liquid has been satisfied, as evidenced by cessation of its heat of wetting.

Bureau of Soils,
Department of Agriculture,
Washington, D. C.

Belated discussion to paper of J. C. Clancy (pages 137-158), received too late for inclusion on page 158.

DISCUSSION.

MR. J. C. CLANCY (*Communicated*): "I doubt the practicability of this process, because its complexity makes it too costly even if effective."

It would appear from the above statement that Dr. Keith has not seen the simplicity of the Clancy process, inasmuch as the only additional chemical used after the solution has once been made up to working strength is cyanamide; the other chemicals making up the working solution are continuously formed in the treatment of ore by the ordinary cyanide solution. The consumption of alkaline iodide is merely the mechanical loss, about 8 percent of the total iodide.

Dr. Keith again refers to the use of blankets as obsolete practice, but if he would inspect the three modern cyanide mills in Colorado Springs, Colo., viz.: the Portland, Golden Cycle and U. S. Reduction Co., treating Cripple Creek ores, he would find that each of the said mills uses blankets as a cheap and efficient means of rough concentration after roasting.

To go into the meaning of "protective alkalinity" is platitudinous; it is sufficient to state that if Dr. Keith will take the trouble to look up any of the modern text books on cyanidation he will find that it is a term much used and standardized in cyanidation.

I have already stated in my paper that cyanogen iodide may be formed in a solution containing 0.1 to 0.2 lb. "protective alkalinity" per ton of solution.

Concerning regeneration of cyanide, if Dr. Keith will look up the standard works on the electrolysis of cyanide solution he will find that cyanate is formed by the electrolysis of cyanide and, once formed, cannot be regenerated from the latter compound. Another point: in using oxidation agents in the cyanide solution, cyanate is always formed.

"The use of sodium chloride in the solvent * * * * it would become loaded with salts." In answer to this criticism, chlorine does not escape into the air, cite for example, the electrolysis of sodium chloride in the manufacture of sodium hypochlorite.

The increase of alkalinity is taken care of by the increase of

acidity due to the oxidation KCNS and sulphides, as already described in my paper. The working solution being increased in alkalinity towards the finish, after passing the zinc it is ready for the treatment of another batch of ore. The fresh batch of ore will require alkali to neutralize its acidity; consequently, any increase of alkalinity due to electrolysis and the added alkali will augment in this neutralization. In this way any excess alkalinity is eliminated. This is the method practiced on the working scale and will surely answer Dr. Keith's objections.

The question of precipitation of gold on the cathode is negligible, as it is redissolved as soon as the current is stopped, and being deposited in a very loose powdery form is brushed off by the motion of the pulp and enters solution. The deposition of zinc on the cathode is too remote to be considered, as well as from well-known electrochemical reasons.

INDEX

PAGE

Accumulator Plate, The Tate Bifunctional—Alfred O. Tate..... 47
Address, Presidential; Chemical Research and Industrial Progress—Wm. H. Walker 17
Advantages of Keokuk, Iowa, for Electrochemical Industries—Frank P. H. Knight 345
Advantages of Maine for Electrochemical Industries—C. Vey Holman. 351
A Few Experiences with the 15-Ton Heroult Electric Furnace at South Chicago—C. G. Osborne 205
Alumina, Electrically Fused (Alundum) as a Refractory—L. E. Saunders 333
Aluminium, Some Observations on Laboratory Production of—H. K. Richardson 159
"Alundum" (Alumina Electrically Fused) as a Refractory— L. E. Saunders 333
Amalgamating Gold Ores, The Electrolytic System of—Elmer Ellsworth Carey 127
An Electric Furnace for Heating Bars and Billets—Thaddeus F. Baily. 285
An Electrolytic Furnace Method for Producing Metals—John Woods Beckman 171
A New Electric Resistance Furnace—Francis A. J. FitzGerald..... 273
A New Type of Electric Furnace—Carl Hering 255
Annual Report of Board of Directors 8
Annual Report of the Secretary 9
Annual Report of the Treasurer..... 12
Assistant Secretary, Appointment of..... 8
Baily, Thaddeus F.—An Electric Furnace for Heating Bars and Billets. 285
Baily, Thaddeus F.—*Discussions*..... 231, 295 *et seq.*
Baker, C. E.—*Discussion* 184
Bars and Billets, An Electric Furnace for Heating—Thaddeus F. Baily. 285
Beckman, John Woods—An Electrolytic Furnace Method for Producing Metals 171
Beckman, John Woods—*Discussions* ..... 176 *et seq.*, 265, 342
Bentley, W.—*Discussion* 184
Bessemer and Open Hearth, Electric Steel Processes as Competitors of —Albert E. Greene 233
Bifunctional Accumulator Plate, The Tate—Alfred O. Tate..... 47
Billets and Bars, An Electric Furnace for Heating—Thaddeus F. Baily. 285
Bleecker, W. F.—*Discussions* ..... 176 *et seq.*, 315 *et seq.*
Bregowsky, Mr.—*Discussion* 191
Brown, Dr. J. W.—*Discussions*..... 52, 64

PAGE
Burgess, Charles F.—*Discussion* ..... 183 *et seq.*
Burgess, Charles F.—Electrolytic Refining as a Step in the Production of Steel 181
Carey, Elmer Ellsworth—*Discussion* 135
Carey, Elmer Ellsworth—The Electrolytic System of Amalgamating Gold Ores 127
Carrier, C. F.—*Discussion* 284
Cells, Dry, Testing of—W. B. Pritz 31
Chemical Research and Industrial Progress—Wm. H. Walker 17
Chicago Local Section Authorized 8
Clamer, G. H.—*Discussion* 263
Clancy, John Collins—*Discussion* 381
Clancy, John Collins—The Clancy Electrochemical Cyanide Process 137
Clerc, F. L.—*Discussion* 331
College of the City of New York, Laboratory 5
Columbia University Laboratory 5
Commercial Work, The Reliability of Electric Furnaces for—Fred T. Snyder 185
Competitors of the Bessemer and Open Hearth, Electric Steel Processes as—Albert E. Greene 233
Condensation of Zinc Vapor from Electric Furnaces—F. T. Snyder 317
Corrosion, Electrolytic, of Electroplated Objects—Walter S. Landis 59
Cowles, A. H.—*Discussions* ..... 122 *et seq.*, 167 *et seq.*
Cyanide Process, Clancy Electrochemical—J. C. Clancy 137
Decomposition Pressure of Electrolytes, Relation of Polarization to—Oliver P. Watts 91
Directors, Annual Report of the Board of 8
Discharges, Electric, in Gases at Reduced Pressure—Louis A. Parsons 109
Dry Cell Testing—W. B. Pritz 31
Election, Report of the Tellers 2
Electrical Heating as a Means of Prevention of Superheating of Liquids—J. Howard Mathews 81
Electrically Fused Alumina (Alundum) as a Refractory—L. E. Saunders 331
Electric Discharges in Gases at Reduced Pressure—Louis A. Parsons 109
Electric Furnace, A New Type of—Carl Hering 255
Electric Furnace at South Chicago, A Few Experiences with the Heroult—C. G. Osborne 205
Electric Furnace for Heating Bars and Billets, An—Thaddeus F. Baily 285
Electric Furnace for the Manufacture of Iron and Steel, The—James Lyman 193
Electric Furnaces, Reliability of, for Commercial Work—Fred T. Snyder 185
Electric Furnaces, The Condensation of Zinc Vapor from—Fred T. Snyder 317

PAGE
Electric Heating Apparatus, A Replaceable Unit System of—M. M. Kohn 299
Electric Resistance Furnace, A New—Francis A. J. FitzGerald..... 273
Electric Steel Processes as Competitors of the Bessemer and Open Hearth—Albert E. Greene 233
Electric Zinc Furnace, The Johnson—J. W. Richards 311
Electrochemical Cyanide Process, The Clancy—J. C. Clancy..... 137
Electrochemical Industries, The Advantages of Keokuk, Iowa, for—Frank P. H. Knight 345
Electrochemical Industries, The Advantages of Maine for—C. Vey Holman 351
Electrochemistry, Relation of Surface Action to—Harrison E. Patten..359
Electrolytes, Polarization in its Relation to the Decomposition Pressure of—Oliver P. Watts 91
Electrolytic Corrosion of Electroplated Objects, The—Walter S. Landis. 59
Electrolytic Furnace Method for Producing Metals, An—John Woods Beckman 171
Electrolytic Meter, Mercurous Perchlorate—Frank C. Mathers and Albert F. O. Germann 69
Electrolytic Refining as a Step in the Production of Steel—Charles F. Burgess 181
Electrolytic System of Amalgamating Gold Ores, The—Elmer Ellsworth Carey 127
Electrolytic Transfer, The Mechanism of—J. W. Richards..... 119
Electroplated Objects, The Electric Corrosion of—Walter S. Landis... 59
Electroplating, Some Unsolved Problems in—George B. Hogaboom.... 53
Experiences with the 15-Ton Heroult Electric Furnace at South Chicago—C. G. Osborne 205
Financial Statement 11
FitzGerald, F. A. J.—A New Electric Resistance Furnace..... 273
FitzGerald, F. A. J.—*Discussions* 191, 284, 339
Furnace, A New Electric Resistance—F. A. J. FitzGerald..... 273
Furnace, Electric, A Few Experiences with the 15-Ton Heroult at South Chicago—C. G. Osborne 205
Furnace, Electric, A New Type of—Carl Hering..... 255
Furnace, Electric, for Heating Bars and Billets—Thaddeus F. Baily...285
Furnace, Electric, for the Manufacture of Iron and Steel—James Lyman 193
Furnace Method, An Electrolytic, for Producing Metals—John Woods Beckman 171
Furnace, The Johnson Electric Zinc—J. W. Richards 311
Furnaces, Electric, The Condensation of Zinc Vapor from—Fred T. Snyder 317
Furnaces, Electric, Their Reliability for Commercial Work—Fred T. Snyder 185

PAGE
Fused Alumina (Alundum) as a Refractory—L. E. Saunders.....333
Gases at Reduced Pressure, Electric Discharges in—Louis A. Parsons.109
Germann, Albert F. O., and Frank C. Mathers—Mercurous Perchlorate Electrolytic Meter 69
Gold Ores, The Electrolytic System of Amalgamating—Elmer Ellsworth Carey 127
Greene, Albert E.—*Discussion* .....251 *et seq.*
Greene, Albert E.—Electric Steel Processes as Competitors of the Bessemer and Open Hearth.....233
Guests Registered at the Nineteenth General Meeting 14
Hansen, C. A.—*Discussions* .....175, 223 *et seq.*, 341, 351
Hanson and Van Winkle Company 5
Heating Apparatus, Electric, A Replaceable Unit System of—Milton H. Kohn 299
Heating Bars and Billets, An Electric Furnace for—Thaddeus F. Baily.285
Heating, Electrical, as a Means of Prevention of Superheating of Liquids—J. Howard Mathews 81
Hering, Carl—A New Type of Electric Furnace.....255
Hering, Carl—*Discussions*, 64, 79, 106 *et seq.*, 170, 179, 231, 265 *et seq.*, 297, 341.
Heroult Electric Furnace at South Chicago, A Few Experiences with the—C. G. Osborne 205
Hess, Henry—*Discussions* 226, 267
Hibbard, H. D.—*Discussions* 231, 252
Hitchcock, H. K.—*Discussions* 267, 297
Hogaboom, George B.—Some Unsolved Problems in Electroplating.... 53
Hogaboom, George B.—*Discussions* .....56 *et seq.*, 65
Holman, C. Vey—The Advantages of Maine for Electrochemical Industries 351
Industries, Electrochemical, The Advantages of Keokuk, Iowa, for—Frank P. H. Knight 345
Industries, Electrochemical, The Advantages of Maine for—C. Vey Holman 351
International Committee on Units, Appropriation for..... 8
Iron and Steel, The Electric Furnace for the Manufacture of—James Lyman 193
Johnson Electric Zinc Furnace, The—J. W. Richards.....311
Jones, G. H.—*Discussion* 183
Keith, N. S.—*Discussions* 135, 158
Kemery, P.—*Discussion* 268
Keokuk, Iowa, Advantages of, for Electrochemical Industries—Frank P. H. Knight 345
Knight, Frank P. H.—The Advantages of Keokuk, Iowa, for Electrochemical Industries.....345
Kohn, Milton M.—A Replaceable Unit System of Electric Heating Apparatus 299

PAGE
Kohn, Milton M.—*Discussions* .....57, 306 *et seq.*
Laboratory Production of Aluminium, Some Observations on—H. K. Richardson 159
Landis, Walter S.—Assistant Secretary 8
Landis, Walter S.—*Discussion* 67
Landis, Walter S.—The Electrolytic Corrosion of Electroplated Objects. 59
Langmuir, I.—*Discussion* .....229 *et seq.*
Lidbury, F. A.—*Discussions*.....56, 169 *et seq.*, 228, 297, 340
Liquids, Superheating of, Electrical Heating as Means of Prevention—J. Howard Mathews..... 81
Local Section Authorized, Chicago..... 8
Lyman, James—The Electric Furnace for the Manufacture of Iron and Steel 193
Maine, Advantages of, for Electrochemical Industries—C. Vey Holman.351
Manufacture of Iron and Steel, The Electric Furnace for—James Lyman 193
Mathers, Frank C., and Albert F. O. Germann—Mercurous Perchlorate Electrolytic Meter 69
Mathers, Frank C.—*Discussion* 80
Mathews, J. Howard.—*Discussion* 90
Mathews, J. Howard—Electrical Heating as a Means of Prevention of Superheating of Liquids 81
Maywald, Dr. F. J.—Laboratory 5
McCoy, H. N.—*Discussion* 183
Means of Prevention of Superheating of Liquids, Electric Heating as a—J. Howard Mathews 81
Mechanism of Electrolytic Transfer, The—J. W. Richards.....119
Members and Guests Registered at the Nineteenth General Meeting... 12
Members Elected and Qualified..... 15
Membership, Condition of the Society in 1910 as to..... 10
Mercurous Perchlorate Electrolytic Meter—Frank C. Mathers and Albert F. O. Germann 69
Metals, An Electrolytic Furnace Method for Producing—John Woods Beckman 171
Meter, Electrolytic, Mercurous Perchlorate; Frank C. Mathers and Albert F. O. Germann 69
Metric Equivalents to Be Given in These Transactions 8
Minutes of the Nineteenth General Meeting..... 1
Moss Engraving Company, Plant of 5
New Electric Resistance Furnace, A—Francis A. J. FitzGerald.....273
New Members, Elected and Qualified 15
New Type of Electric Furnace, A—Carl Hering.....255
New York Electrical Testing Laboratory 5
Observations on Laboratory Production of Aluminium—H. K. Richardson 159

PAGE
On the Relation of Surface Action to Electrochemistry—Harrison E. Patten 359
Open Hearth, Electric Steel Processes as Competitors of Bessemer and —Albert E. Greene 233
Ores, Gold, The Electrolytic System of Amalgamating—Elmer Ellsworth Carey 127
Osborne, C. G.—A Few Experiences with the 15-Ton Heroult Electric Furnace at South Chicago 205
Osborne, C. G.—*Discussion* ..... 222 *et seq.*
Parsons, Louis A.—*Discussion* 121
Parsons, Louis A.—Electric Discharges in Gases at Reduced Pressure. 109
Patten, Harrison E.—*Discussion* ..... 306 *et seq.*
Patten, Harrison E.—On the Relation of Surface Action to Electrochemistry 359
Polarization in its Relation to the Decomposition Pressure of Electrolytes—Oliver P. Watts 91
Presidential Address; Chemical Research and Industrial Progress—Wm. H. Walker 17
Prevention of Superheating of Liquids, Electrical Heating as a Means of—J. Howard Mathews 81
Pritz, W. B.—Dry Cell Testing 31
Problems in Electroplating, Some Unsolved—George B. Hogaboom... 53
Proceedings of the Nineteenth General Meeting 1
Production of Aluminium in Laboratory, Some Observations on—H. K. Richardson 159
Production of Metals, An Electrolytic Furnace Method for—John Woods Beckman 171
Production of Steel, Electrolytic Refining as a Step in the—Charles F. Burgess 181
Queneau, A. L. J.—*Discussions* 230, 268, 315, 343
Reduced Pressure, Electric Discharges in Gases at—Louis A. Parsons.. 109
Refining, Electrolytic, as a Step in the Production of Steel—Charles F. Burgess 181
Refractory, Electrically Fused Alumina (Alundum) as a—L. E. Saunders 333
Relation of Polarization to Decomposition Pressure of Electrolytes—Oliver P. Watts 91
Relation of Surface Action to Electrochemistry—Harrison E. Patten..359
Reliability of Electric Furnaces for Commercial Work, The—Fred T. Snyder 185
Replaceable Unit System of Electric Heating Apparatus, A—M. M. Kohn 299
Report of Board of Directors, Annual 8
Report of Secretary, Annual 9
Report of the Tellers of Election 2

PAGE
Report of the Treasurer, Annual 12
Resistance Furnace, A New Electric—Francis A. J. FitzGerald.....273
Richards, J. W.—*Discussions*..62 *et seq.*, 106, 124, 166 *et seq.*, 177, 223 *et seq.*, 265, 295 *et seq.*, 308, 315 *et seq.*, 343.
Richards, J. W.—The Johnson Electric Zinc Furnace.....311
Richards, J. W.—The Mechanism of Electrolytic Transfer.....119
Richardson, H. K.—*Discussion* 90
Richardson, H. K.—Some Observations on Laboratory Production of Aluminium 159
Saunders, L. E.—*Discussions*.....178, 223 *et seq.*, 265, 339 *et seq.*
Saunders, L. E.—Electrically Fused Alumina (Alundum) as a Refractory 333
Schleuderberg, C. G.—*Discussion*.....78 *et seq.*
Secretary, Annual Report of the 9
Secretary, Assistant, Prof. W. S. Landis 8
Sharp, Clayton H.—*Discussion*..... 79
Smith, A. W.—*Discussion* 123
Snyder, F. T.—*Discussions*.....183, 191, 331
Snyder, F. T.—The Condensation of Zinc Vapor from Electric Furnaces 317
Snyder, F. T.—The Reliability of Electric Furnaces for Commercial Work 185
Some Unsolved Problems in Electroplating—George B. Hogaboom.... 53
South Chicago, A Few Experiences with the 15-Ton Heroult Electric Furnace at—C. G. Osborne 205
Sperry, E. A.—*Discussion* 297
Steel and Iron, The Electric Furnace for the Manufacture of—James Lyman 193
Steel, Electrolytic Refining as a Step in the Production of—Charles F. Burgess 181
Steel Processes, Electric, as Competitors of the Bessemer and Open Hearth—Albert E. Greene.....233
Strong, A. H.—*Discussion* 268
Superheating of Liquids, Electrical Heating as a Means of Prevention of—J. Howard Mathews..... 81
Surface Action, Relation of, to Electrochemistry—Harrison E. Patten..359
System, of Amalgamating Gold Ores, The Electrolytic—Elmer Ellsworth Carey 127
System, Replaceable Unit, of Electric Heating Apparatus—M. M. Kohn.299
Tate, Alfred O.—*Discussion* 52
Tate, Alfred O.—The Tate Bifunctional Accumulator Plate..... 47
Tellers of Election, Report of the..... 2
Testing of Dry Cells—W. B. Pritz..... 31
The Advantages of Keokuk, Iowa, for Electrochemical Industries—Frank P. H. Knight 345

PAGE
The Advantages of Maine for Electrochemical Industries—C. Vey Holman 351
The Clancy Electrochemical Cyanide Process—John Collins Clancy.... 137
The Condensation of Zinc Vapor from Electric Furnaces—Fred T. Snyder 317
The Electric Furnace for the Manufacture of Iron and Steel—James Lyman 193
The Electrolytic Corrosion of Electroplated Objects—Walter S. Landis. 59
The Electrolytic System of Amalgamating Gold Ores—Elmer Ellsworth Carey 127
The Johnson Electric Zinc Furnace—J. W. Richards..... 311
The Mechanism of Electrolytic Transfer—J. W. Richards..... 119
The Reliability of Electric Furnaces for Commercial Work—Fred T. Snyder 185
The Tate Bifunctional Accumulator Plate—Alfred O. Tate 47
Thwing, C. B.—*Discussion* 309
Transfer, Electrolytic, The Mechanism of—J. W. Richards..... 119
Treasurer, Annual Report of the..... 12
Tucker, S. A.—*Discussions*..... 169, 176, 225, 339
Unit System, Replaceable, of Electric Heating Apparatus—M. M. Kohn. 299
Units, International Committee on 8
Unsolved Problems in Electroplating, Some—George B. Hogaboom.... 53
Walker, Wm. H.—*Discussions* 56, 64, 118, 169, 177, 309, 339
Walker, Wm. H.—Presidential Address; Chemical Research and Industrial Progress 17
Watts, Oliver P.—*Discussion* 108
Watts, Oliver P.—Polarization in its Relation to the Decomposition Pressure of Electrolytes 91
Whitney, W. R.—*Discussions* 117, 284, 306, 344
Willard, F. W.—*Discussion* 65
Wolff, F. A.—*Discussion* 66
Worth, B. G.—*Discussion* 267
Zinc Furnace, The Johnson Electric—J. W. Richards..... 311
Zinc Vapor from Electric Furnaces, The Condensation of—F. T. Snyder 317

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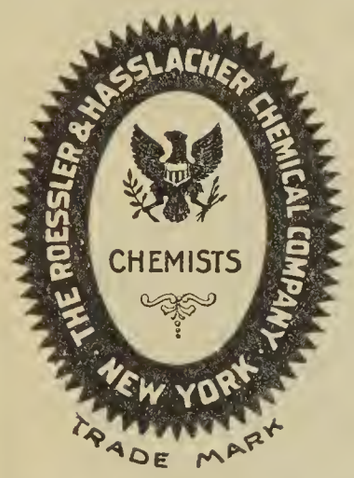

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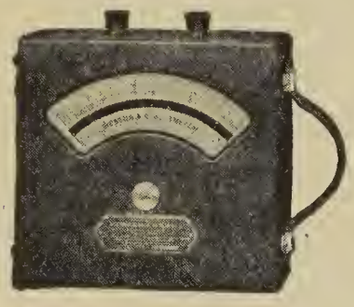

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The compactness of design of the alternating-current induction type instruments, with 14.4 inch scales, improved magnet and movement details, makes these meters an important advance in indicating switchboard instrument construction.

A feature worthy of special mention is the perfectly damped character of the readings. The pointer does not overshoot the mark, nor oscillate, even with full scale variation. This remarkable result is not obtained at the expense of accuracy, but by providing a special damping disc moving in the concentrated magnetic field of two permanent magnets.

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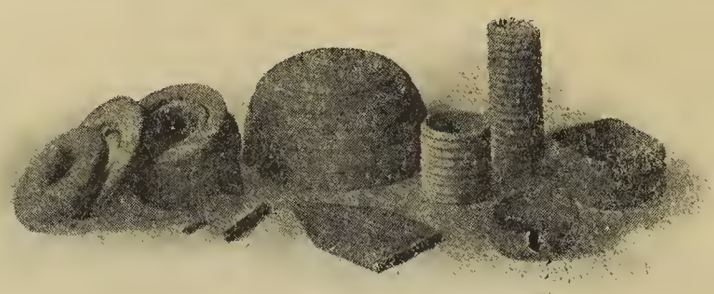

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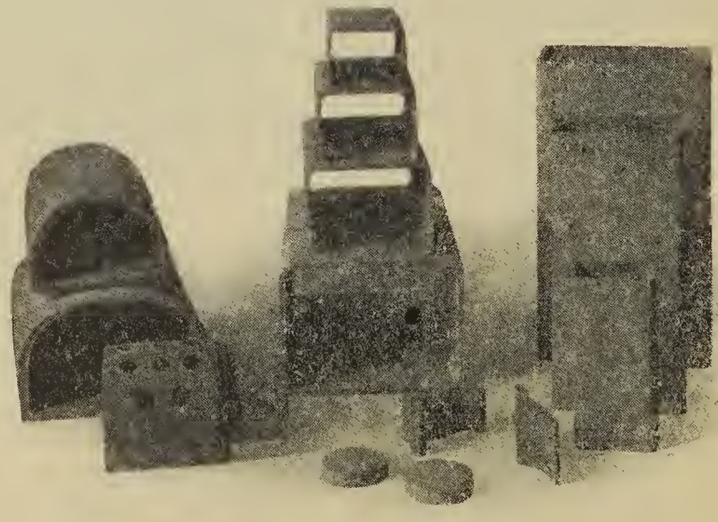
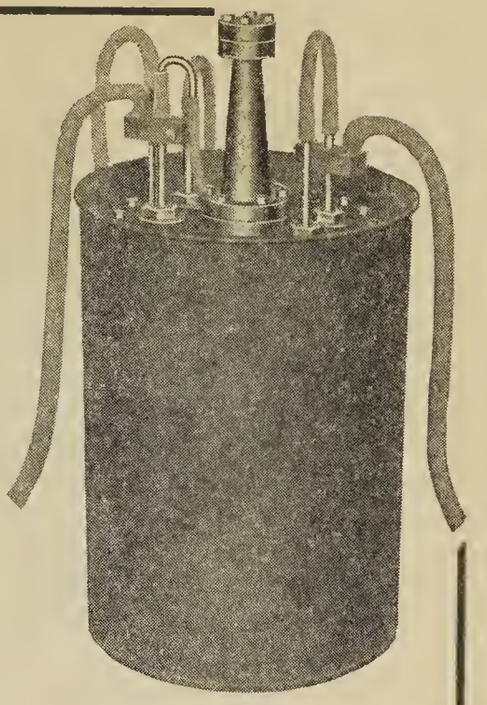


A Valuable Furnace for the Laboratory



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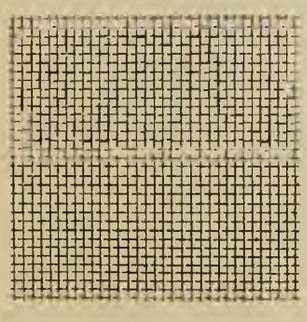

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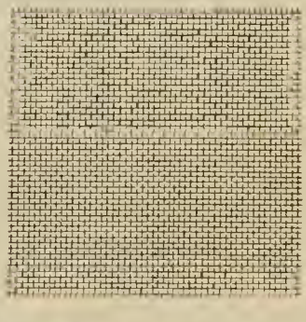

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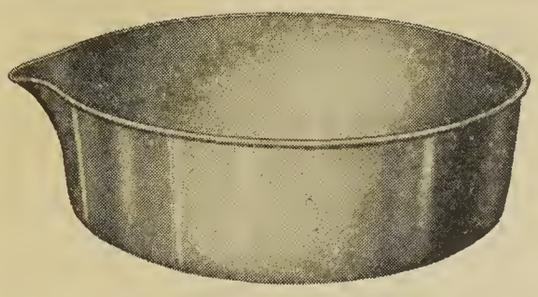

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